

REPORT

Functional Glasses: Properties and Applications for Energy and Information

**January 6 – 11, 2013
Siracusa, Sicily, Italy**

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1. Introduction

“The International Interactive Conference on Functional Glasses: Properties and Applications for Energy & Information” took place on January 6-11, 2013 in Siracusa, Sicily. The organization and funding of this unique conference were the result of a multi-year effort by the “NSF’s International Materials Institute for New Functionality in Glass (IMI-NFG)” to bring together active glass researchers with the industries using or manufacturing glass for innovative new products. The meeting was organized unlike most regular or topical conferences in order to promote extensive discussion amongst academics, technologists and manufacturers: invited speakers only, defined discussion leaders, an industry panel, a detailed summary report and a roadmap outlining future needs and opportunities for glass in these technologies. The format of the conference was somewhat like at Gordon Conferences, consisting of 45-minute overview talks followed by 30-minutes of discussion led by a leader in the field. Any contributed new work was presented as posters.

After the opening remarks by Himanshu Jain, the conference started with high level overviews of important applications and challenges from the engineering and manufacturing segments for glasses used in energy and information technologies (see Table 1). The rest of the conference aimed to define the resulting technical challenges for the materials and to identify scientific issues pertaining to the relevant phenomena. The high level invited keynote speakers reported on selected specific topics most relevant to the two technologies. They were requested to provide a broad overview and help the audience recognize the main scientific issues and engineering challenges in sufficient detail. Thus the talks generated enthusiasm and prepared the audience to discuss the issues under a Discussion Leader and to collectively establish the agenda for future studies in respective fields.

Table 1: List of presentation titles, speakers and discussion leaders.

Presentation Title	Speaker	Discussion Leader
Integrated Glass Substrates for OLED Lighting	Mehran Arbab, PPG Industries Inc., USA	Klaus Bange, MK Consulting, GmbH, Germany
High Refractive Index Glass for OLED Lighting	Takashi Murata, Nippon Electric Glass (NEG), Japan	Şener Oktik, Şişecam, Turkey
Photovoltaic Industry & Role of Glass for Reducing the Cost of Solar Energy	Şener Oktik, Şişecam, Turkey	Driss Lamine, Saint Gobain, France
A General Introduction for the Use and Needs of TCMs	Driss Lamine, Saint-Gobain Recherche, France	Claes-Goran Granqvist, Uppsala Uni., Sweden
Ultra-Slim Glass for Electronic Applications	Sean Garner, Corning, USA	Richard Brow, Missouri University of S & T,

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		USA
Alterations of Glass Surfaces & Functional Coatings for Energy Conversion Systems	Joachim Deubener, Clausthal University, Germany	Roland Langfeld, SCHOTT AG, Germany
Sealing Glasses for Electrochemical Devices	Richard Brow, Missouri Uni. of Sci. & Techn., USA	Joachim Deubener, Clausthal University, Germany
Coated Glass for Energy Efficient Buildings: Spectral selectivity, angular dependence & time variability	Claes-Goran Granqvist, Uppsala University, Sweden	Philip Russell, Max Planck, Germany
Dielectric Properties of Glasses & Glass Ceramics and Examples of Applications	Martin Letz, SCHOTT AG, Germany	Minoru Tomozawa, Rensselaer Polytechnic Institute, USA
Fundamentals of Indentation Cracking in Glass: A measure of strength?	Satoshi Yoshida, University of Shiga Prefecture, Japan	Rene Gy, Saint Gobain Research, France
Sharp Contact Damage in Ion-exchanged Cover Glass	Timothy Gross, Corning, USA	Tayyab Suratwala, Lawrence Livermore Nat'l Lab, USA
Surface Chemistry of Glass: Interfacial Water & Mechanochemical Properties	Seong Kim, Pennsylvania State University, USA	Takashi Murata, Nippon Electric Glass (NEG), Japan
Glasses for Energy Storage: Advancing the Energy Density and Safety of Batteries	Steve W. Martin, Iowa State University, USA	Monia Montorsi, University of Modena, Italy
Glass-Ceramics for the Innovative Secondary Batteries	Tsuyoshi Honma, Nagaoka Uni. of Technology, Japan	Lisa Klein, Rutgers University, USA
Ion Transport Across Grain Boundaries in Fast Lithium Ion Conducting Glass Ceramics	Bernhard Roling, University of Marburg, Germany	Steve W. Martin, Iowa State University, USA
Proton Behavior at Glass/Water Interfaces: Implications on Reactions & Proton Transport	Stephen H. Garofalini, Rutgers University, USA	Jincheng Du, Uni of North Texas, USA
Glass and Glass Ceramic for Non-linear Optics: Fundamentals to Applications	Thierry Cardinal, University of Bordeaux, France	Mario Affatigato, Coe College, USA
Phase-Change Materials: Trends &	Yong Gyu Choi,	Himanshu Jain, Lehigh

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Prospects	Korea Aerospace Uni., Korea	University, USA
Micro-modification of Glass by Femtosecond Laser: Fundamentals & Applications	Jianrong Qiu, South China Uni. of Technology, China	Denise Krol, University of California-Davis, USA
Microstructured Optical Fibers: Opportunities and Challenges	Philip Russell, Max Planck, Germany	Younès Messaddeq, Université Laval, Canada
Microfiber & Nanofiber Photonics	Limin Tong, Zhejiang University, China	Octavio Cintora, Saint Gobain, France
Photosensitivity of Optical Materials for Photonics and Integrated Optics	Raman Kashyap, Ecole Polytechnique de Montreal, Canada	Denise Krol, University of California-Davis, USA
Towards the Development of New Optical Fibers	Younès Messaddeq, Université of Laval, Canada	Jianrong Qiu, South China Uni. of Technology, China
Making Glass Better	Roland Langfeld, SCHOTT AG, Germany	Setsuro Ito, Tokyo Institute of Technology, Japan
Surface Interactions on Glass Optics during Fabrication, Post-processing & Laser Operation	Tayyab Suratwala, Lawrence Livermore National Lab, USA	Raman Kashyap, University of Montreal, Canada
Production of Chalcogenide Glass Optics: Motivation, Current Status and Future Developments	Xiang-Hua Zhang, University of Rennes, France	Akihiko Sakamoto, Nippon Electric Glass (NEG), Japan
Unlimited Glass - A Mirror of Our World's Trends	Marc van den Neste, Asahi Glass-Europe	Dinner Presentation
Path to the Realization of "A Day Made of Glass"	M.K. Badrinarayana, Corning, USA	Dinner Presentation

The abstracts of the talks were provided to all speakers before they finalized their presentation in the hope that their talks would fill the gaps of relevant knowledge, avoid duplication, and address the possible role of their fundamentals in meeting the application needs. The Discussion Leaders were provided a questionnaire (see Appendix) before the conference to organize the flow of discussion, and to have a pre-conference dialog with his or her Keynote Speaker. The Discussion Leaders also prepared a summary of the discussion, which is incorporated in this report. At the end of the conference a panel discussion led by participating industrial leaders reviewed, ranked and evaluated the various issues identified during the week.

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The ~80 participants (including 28 invited speakers and corresponding invited discussion leaders) from 15 countries represented academia and industry in comparable number. The technical program, which focused primarily on energy and information technologies, was organized according to the following structure:

- Applications of glass in energy technology
- Applications of glass in information technology
- Glass properties for energy applications
- Energy storage technologies
- Glass properties for information applications
- Glass processing and fabrication

This report summarizes the main message of the different talks and the subsequent interactive discussions. It also attempts to evaluate and identify the most critical needs and scientific issues in the two fields. For more in-depth discussion of specific issues, most important key topics of each session have been summarized and displayed in the format of roadmaps at the end of each Section. It is hoped that further discussion of these topics will be taken up at future workshops and topical meetings.

2. Glasses in Energy Technology

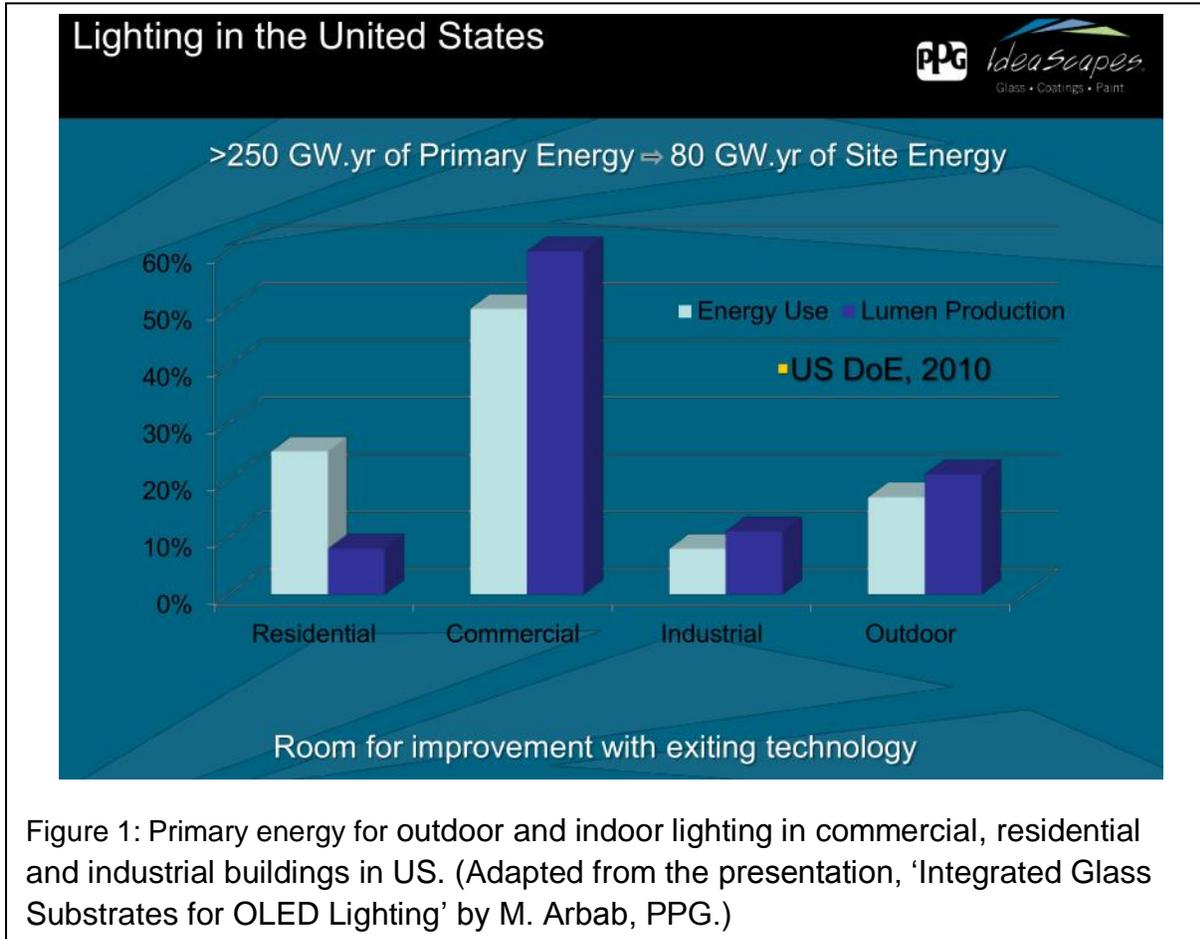
The ranking of the “energy” in the priority list of different countries has moved up significantly in recent years worldwide, and an increasing number of new energy technologies are entering the marketplace. For many of these energy technologies glass is “the” enabler. This is well known in the energy generation sector, e.g. in photovoltaic (PV) and concentrated solar power (CSP) applications, but for other applications like in energy storage or energy conservation also there is potential for more advanced applications of glass.

This section is divided into four subsections: Applications of Glass in Energy Technology; Glass Properties for Energy Applications; Energy Storage Technologies; and summary of the findings at the end in the format of roadmaps (sect 2.4).

2.1. Applications of Glass in Energy Technology

The status and potential of the current and future glass applications are illustrated by the selected examples of organic light-emitting diode (OLED) lighting, PV and energy conversion systems. These topics are described and discussed as follows:

In the first session of the conference, Mehran Arbab (PPG Industries, USA) gave a presentation on “**Integrated glass substrates for OLED lighting**”. He pointed out to a US Department of Energy report, which indicated that in 2010 outdoor and indoor lighting in commercial, residential and industrial buildings consumed more than 250 GWy of primary energy in the United States. This has motivated research and development of new lighting technologies and new legislation to progressively redirect incandescent lighting to fluorescent, compact fluorescent, and solid state light emitting diode lighting technologies. A lighting concept appearing on the horizon is based on the organic light emitting diode (OLED) technology that has already gained traction in the display market with leading electronics companies investing in research and capital in OLED screens. The fundamentals of OLED lighting are compelling: high efficiency and



low environmental footprint. However, cost remains an issue, but glass technology can significantly impact its commercial success. High transparency glass combined with low cost transparent conductive coatings and light extraction technologies may lead to efficient, low cost and long service-life devices. If successful, this can become a new commercial opportunity for the flat glass industry.

Key statements of the talk were “light is everywhere”, which means the markets are huge and offer greatest opportunity for change since the time of Edison; “Glass has a long tradition in lighting applications”, i.e. producers of lighting products, such as light bulbs, are used to working with glass – both should be seen as an advantage. However, future lighting products have to produce photons more efficiently, i.e. with less electrons/current to reduce the energy consumption. Since lighting products are commodity products and serve mass markets, they have to be cheap. Besides the cost issues, the main glass technology challenges are in the area glasses with higher refractive index, large area coatings with transparent conducting oxide (TCO) materials, organic layers and metal films, structuring of large areas of glass, and encapsulation to avoid contact to water and oxygen containing species. In this regard, the low permeability of water and oxygen through glass (and oxide thin films) gives glass a major advantage over plastics. In addition, glass surface modifications to increase the light extraction from the OLED device, and longer life times than the currently used lighting technique increase the probability for a successful market entrance. The

concept of “integrated glass substrate” seems to be an interesting approach for a flat glass producer to support the lighting industry and to participate on a fast growing market in the future.

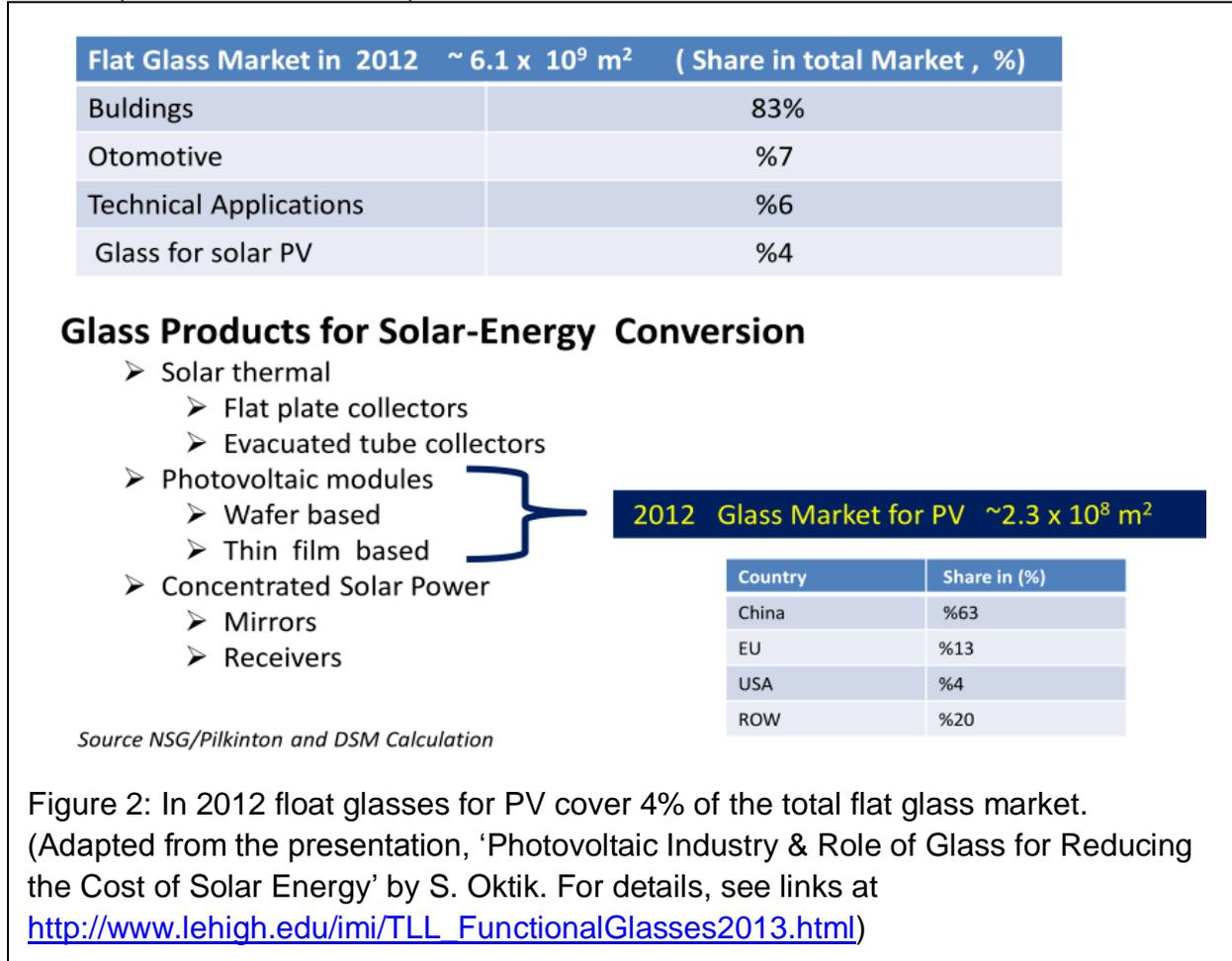
The current status of another important application of glass in the energy technology was summarized by Sener Oktik (Sisecam, Turkey) in a talk titled **“Photovoltaic industry and role of glass for reducing the cost of solar energy”**. Photovoltaic conversion of sunlight into electricity is a versatile process that currently contributes to world energy demand moderately. There have been significant research and technological development (RTD) efforts at every stage of the photovoltaic value chain across the world. Over the last two decades, appreciable technological improvements and sustained growth in production volume have resulted in price reduction beyond expectations. This in turn has made photovoltaic power the third most important renewable energy source after hydro and wind powers. Photovoltaic power systems (PVPS) connected to the grid have increased from about 17GWp (2010) to almost 30GWp (2011) in a year. In 2011, the total global installed PVPS reached ~70GWp producing ~ 85TWh electrical energy, which is equal to the production capacity of 12GW nuclear power plants. Over the years, the West has dominated RTD, materials and components production together with system installation activities in the field of PV. However, in recent years while the major parts of RTD and PVPS installations have remained in the West, production has shifted towards the East. The foreseen price decrease currently being in the PV value chain seems to continue over the medium and long terms. Thus, depending on when and where the correct policies are implemented, photovoltaic power could become more competitive with conventional electrical energy production technologies starting from sun-belt countries.

There are currently many large-scale international efforts for improving the consumer acceptance of PV modules and systems. At the crystalline silicon or thin films module level, performance improvement and cost reduction are the primary targets. Over the last decade, efficiencies of the best crystalline silicon cells, CuIn(Ga)S(Se) i.e. CIGS cells, CdTe cells, and thin film silicon cells have improved by 5.5%, 4.6%, 5.1% and 3.9%, respectively. There has also been notable progress in the technology to stabilize crystalline and thin film modules. In an attempt to reduce cost of per Wp in photovoltaic conversion, an improvement of cell efficiency is just one parameter, and the main cost factors related to all production materials and technologies need to be considered.

Glass is used in crystalline photovoltaic module as a protective and supporting layer, but in thin film modules glass also serves as the substrate or superstrate. In a recent evaluation, the relative cost fraction of glass is about 10% in crystalline Si modules and almost 25% in thin film modules. Recent estimates for the total material cost of a 0.24€/Wp for CIGS modules is dominated by the cost of glass (0.10€/Wp).¹ Thus research and technological developments in glass for PV play a major role in the future of the photovoltaic industry.

The presentation aimed on the discussion of the status and future prospects of the photovoltaic value chain together with the role of glass and glass RTD for photovoltaic module production. Accordingly, suitable technological developments will be required in production and coatings processes for improved optical, mechanical and chemical properties of PV glasses parallel to RTD activities in float glass, despite the

fact that PV glass covers only a small fraction ($\sim 8 \times 10^7 \text{ m}^2$ in 2010) of the flat glass market ($5.5 \times 10^9 \text{ m}^2$ in 2010) – see below:²



Despite the growing economy, which is combined with an increasing demand for energy, the chronic overcapacity in the worldwide PV production led to profitless prosperity in the year 2012. Since currently the material cost of PV modules is dominated by flat glass, measures for cost reductions are in the focus and should be considered for future developments too. In particular for the PV industry, cost effectiveness for solar float glass has to be realized, together with higher transmission, an increased mechanical stability, and higher degree of flatness and homogeneity. Furthermore, an easy application of antireflective coatings, prevention of corrosion layer, a better processability (cutting, grinding and tempering) and an efficient production of large quantities have to be possible.

In 2012 float glass for PV was only 4% ($\sim 2.3 \times 10^8 \text{ m}^2$) of the total float glass market. But this niche is expanding with a high growth rate and needs more scientific and technological attention to support and to improve the PV modules. The main future trends of photovoltaic modules can be summarized as follows:

- Module productions will be shifting to glass systems of larger sizes,

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- The modules will employ thinner glasses (2 mm front and 2 mm back sheets) while maintaining the same performance and mechanical strength as the 4 mm or 3.2 mm glasses,
- Higher efficiency will be needed compared to conventional modules i.e. the optical transmission would be higher than conventional 3.2 mm low-iron glass for solar glass.

In view of these main trends, R&D activities for PV float glasses should concentrate on topics like higher strength flat glass to support the realization thinner modules, and for the improvements in light efficiencies the optical properties like higher transmission materials, anti-reflecting surfaces, patterned surfaces, self-cleaning surfaces should be studied in greater detail. Finally, the electrical properties of TCO should offer space for improvement.

Joachim Deubener (Clausthal University of Technology, Germany) presented a keynote talk entitled “**Alterations of glass surfaces & functional coatings for energy conversion systems**”. He emphasized that transparent coatings on glass are key components of state-of-the-art energy conversion systems such as PV, CSP and solar fuel. Functional performance of the coating relies on persistent chemical and physical material properties enabling efficient energy conversion processes and ensuring long-term service life. Alteration processes of films on glass during processing and service were reviewed. With respect to glass production and prior to any coating step, alterations of bare glass surfaces of semi-finished products as a result of storage and cleaning can have significant impact on subsequent performance of coatings. Following the manufacturing process changes of coated glasses under post-processing conditions were pointed out. He discussed in detail alteration of film materials and glass covers reducing the level of optical quality and affecting mechanical and chemical resistance during service. The issue was accompanied by the interplay between economics, ecology and warranty claims of coated glass products for renewable energies and taking account of European developments for the energy turnaround (“Energiewende”).

After a detailed overview on the current energy situation in Germany and the influence of renewable energy source act on the transformation of the energy system, there appeared to be a lack of recognition of glass applications in several key sectors besides the sector of renewable energy, such as in traditional energy sources. The potential of glassy thick films was discussed for coal power plant and other fossil power applications including biomass-gas applications. It was demonstrated that in particular renewable energy systems offer many opportunities for glass use. After depicting the situation of glasses for solar bio-fuel generation, the role of glass in photovoltaic modules was described; this is summarized next:

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- Glasses for x/p-Si PV systems are mainly structural materials with no critical contribution to module performance. This sector is under extreme price pressure and incremental improvement in the transmission or the stability of glasses cannot justify an increase in price. The main future contributions are not expected by the bulk glass but by coatings and/or surface modification and

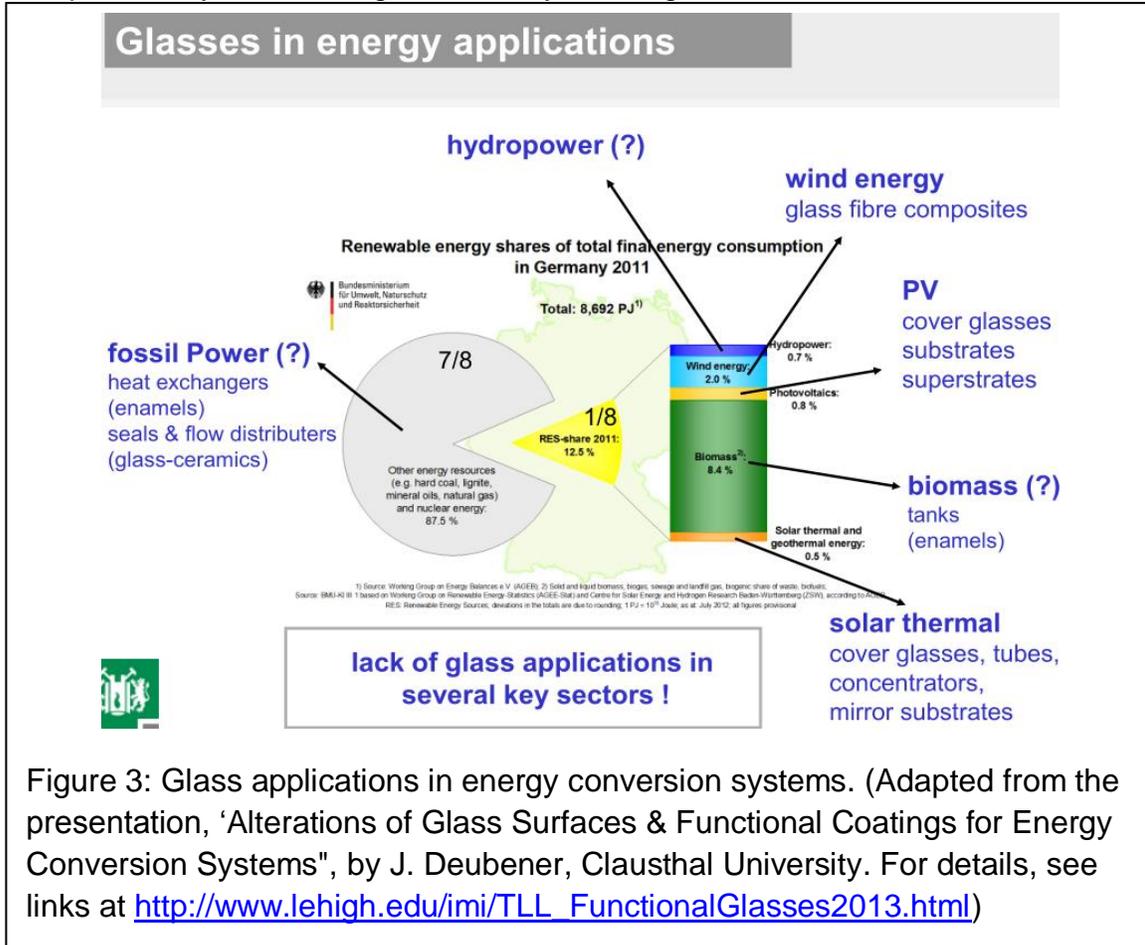


Figure 3: Glass applications in energy conversion systems. (Adapted from the presentation, 'Alterations of Glass Surfaces & Functional Coatings for Energy Conversion Systems', by J. Deubener, Clausthal University. For details, see links at http://www.lehigh.edu/imi/TLL_FunctionalGlasses2013.html)

structuring.

- For CIGS and CdTe based PV, thermally more stable substrates are desired – but maximum tolerable price (increase) is a critical issue. Increasing the performance by 1% justify not more than \$1/m² increase in the price of glass.
- Glasses for concentrated PV are indicated as an interesting application. Higher solar fluxes need glasses that could withstand more intense thermal conditions and solarisation. Extra functions like up/down conversion may become economical because customers are willing to spend more \$ per piece of glass (example: 2nd concentrator)
- For solar thermal power generation, (trough and tower) glasses are on the critical path for the receiver or the entrance window. They would have strong influence on the overall system performance, which may justify somewhat higher

extra costs. Thermally stable, highly transparent glass and AR coatings are the main topics for further improvement.

- For bioreactors, specialty glasses are not required in many cases. However, coating solutions for anti-fouling, better light management and thermal management are of great interest.
- New concepts for power grids (HV-DC technology) require improved high voltage insulators. This could revive interest in glass insulators for this sector.

Fe content in glass establishes a general limit of optical transmission. Reducing Fe content by choosing purer raw materials is an expensive option; smarter ways to deal with its adverse influence on the transmission need to be developed.

2.2 Glass Properties for Energy Applications

Glasses possess some unique properties that are very favorable for applications in the energy technology sector. Two of them, the optical properties and the dielectric properties are treated in greater detail below along with examples and potential in different fields. The first session on glass properties for energy applications discussed the most important optical parameters, in particular for energy saving. Claes-Goran Granqvist (Uppsala University, Sweden) spoke on “**Coated glass for energy efficient buildings: Spectral selectivity, angular dependence and time variability**”. He first presented the radiative properties of our natural surroundings, which are used to define a number of desired performance characteristics for windows to be used in energy efficient buildings. Spectral selectivity, angular dependence, and time variability appeared as key aspects in this regard. The materials options were discussed in detail, and properties of a variety of window coatings were introduced. They include metal films, coatings of heavily doped wide band gap semiconductors, “new carbons”, etc. Special attention was placed on “smart windows”, and the possibilities with electrochromics and thermochromics were considered in detail. The presentation reviewed well-known approaches and techniques, and it also included results from current research and development.

Why bother with buildings & windows

- Global warming
- Increasing sea level
- Increasing CO₂
- Increasing population
- Energy savings are needed
- Buildings use ~40% of all energy
- We spend 80 – 90 % of our time indoors
- Windows are "weak links" in buildings

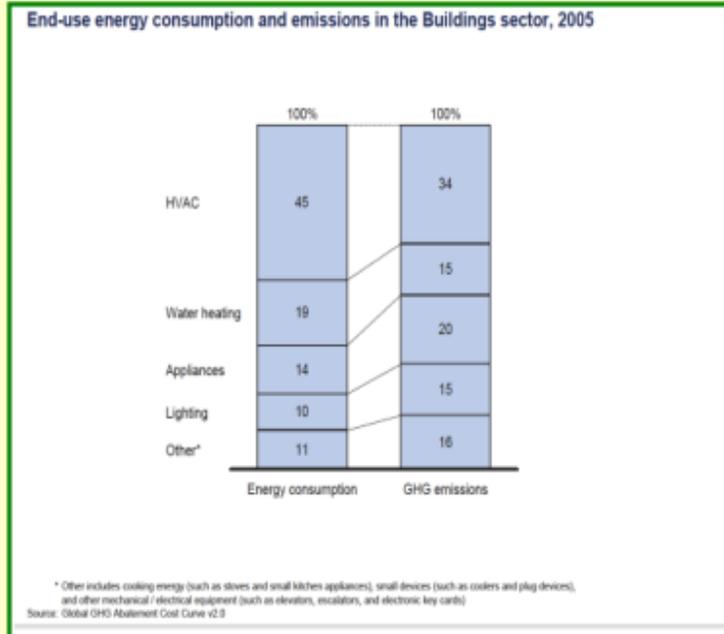


Figure 4: Windows are the weakest part in building insulation. (Adapted from the presentation, 'Coated Glass for Energy Efficient Buildings: Spectral selectivity, angular dependence and time variability', by C. Granqvist, Uppsala University. For details, see links at http://www.lehigh.edu/imi/TLL_FunctionalGlasses2013.html)

Starting with the environmental challenges, the importance to reduce the energy consumption of buildings was addressed, in particular for windows which are the "weak link". The spectral selectivity and electrical conduction in window coatings were described, which can be divided in two principal types related to coatings for solar control and low emittance. The advantages and disadvantages of different material categories were discussed. Heavily doped wide band gap semiconductors like SnO₂:F (FTO), In₂O₃:Sn (ITO), ZnO:Al (AZO), ZnO:Ga (GZO) or TiO₂:Nb exhibit high transmittance and infrared reflectance. Metal systems such as ZnO/Ag/ZnO, TiO₂/Au/TiO₂, ZnO/Ag/ZnO/Ag/ZnO, or acrylic/Ag-Au/acrylic reflect in the near infrared (NIR) part of the spectrum. A relatively new group of transparent conductors is based on carbon nanotubes and meshes (graphene monolayer, C60 "buckyball") which are transparent in NIR.

Windows with changeable optical characteristics exploit chromogenic effects which are

- Photochromic (sensitive to UV light)
- Thermochromic (sensitive to temperature)
- Electrochromic (sensitive to electric field)

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- Gasochromic (sensitive to reducing/oxidizing conditions)

Usually, materials exhibiting such effects are deposited as layers on glass substrate.

Electrochromic (EC) window systems are in the most advanced state and are entering the market. Two specific device designs are available:

- monolithic systems, i.e. all-thin-film systems on glass substrate (sold by Sage/Saint Gobain, Soladigm) and
- laminated systems, i.e. films/laminate/films system on glass or on PET substrate (sold by E-control (glass), GESIMAT (glass), ChromoGenics (PET))

Six main challenges were named for different types of EC devices:

- EC films that are nanocrystalline as well as nanoporous
- Transparent conductor ($\sim 20 \Omega \text{ cm}^{-2}$, $T \approx 90\%$) at low cost
- Charge insertion and balancing that work efficiently
- Electrolyte that has high ion conductivity and UV stability
- Voltage and current control to reach long-term durability
- Large-scale manufacturability for all processes at low cost

Alternative to EC devices include metal hydrides, polymer dispersed liquid crystals, suspended particle devices, reversible electroplating, variable plasmon absorption by transparent and conducting nanoparticles. All these options have the potential for devices with time variable optical properties, but they are in the state of research or development and far away from market launch.

Thermochromic materials are another group of materials for energy efficient windows, especially since just one layer may be sufficient to produce the desired optical performance. Thermochromic crystalline VO_2 shows a switching of optical properties at 68°C , which is too high for windows in buildings. It is IR-transparent and monoclinic at higher temperature, but becomes metallic, IR-reflecting and tetragonal at lower temperatures. The transition state of the material is correlated with the oxidation state. Unfortunately, when trying to shift the switching to occur at lower temperatures, i.e. below 68°C , the films become semiconducting. Evidently, suitable doping of VO_2 can change the transition and hence the optical properties. The luminous transmittance is increased by Mg doping and the transition temperature is decreased by doping with W. Also nanoparticles in the dielectric host of VO_2 influence the optical features of the material

The talk on “**Dielectric properties of glasses and glass ceramics and examples for applications**” was presented by Martin Letz (SCHOTT AG, Germany). In the past, glasses were used in high power electronic applications primarily due to their highly insulating properties even at elevated temperatures. Especially the dielectric breakdown strength of thin glasses is outstanding. Here values up to 1200 kV/mm have been reported. For classical glasses the dielectric constant ranges from $3 < \epsilon' < 25$. This range can be extended to much larger values by expanding to glass-ceramics with ferro- or paraelectric phases. The dielectric loss of glasses especially at GHz frequencies is usually higher than the one of many ceramics or even polymers. Nevertheless the excellent homogeneity of glasses and glass ceramics opens up applications in wireless data transfer working in the GHz range. An extended knowledge of the fundamentals and also a broad overview on the dielectric properties of glasses and glass-ceramic is needed for various potential applications.

The complexity of dielectric concepts pertaining to glasses in definitive applications was illustrated using the example of the glass tubes of backlight discharge external electrode fluorescent lamp (EEFL). Beside the material parameters geometry also affects and electronic issues influence the dielectric characteristics, which should be considered as a part of material development activities. Improved glasses for discharge lamps with capacitive coupling (EEFL) increase lamp efficiency significantly. Ultrathin alkaline free glasses with extremely large breakdown strength for capacitors were described and glass-ceramics for high power capacitors were discussed. Compared with the traditionally used sintered ceramics, glasses have favorable properties in that they are pore-free and homogeneous materials with fewer defects.

Increases in voltage, more IGBT (Insulated-gate bipolar transistor) power electronic, and AC-DC coupling techniques were seen as general trends in the electronics and semiconductor industry. Based on this prediction, more applications for glasses are expected in the following fields in the future:

- High power capacitors need glasses with higher dielectric breakdown strength; pore free and nanostructured glass-ceramics offer advantages over plain ceramics. For DC power transmission, high voltage measurements and high voltage capacitor will be realized. Then phase matching can be an issue.
- In the energy storage applications high power density and high energy density are needed. Then low impurity level (alkali) in dielectrics but also geometry and roughness may become important.
- For high frequency (GHz) applications such as GPS, WLAN, automotive radar and satellite driven microwave electronics, etc., the homogeneity of glasses and glass-ceramics is a great advantage; for wireless communications antenna materials with low dielectrics loss and high dielectric constant at GHz frequencies are needed.

2.3 Energy Storage Technologies

Ion conduction in glass as solid state electrolyte is of general interest for the development of safer and higher energy density batteries. Lithium batteries in the market today utilize flammable organic liquid electrolytes to conduct lithium ions at high rate between the anode and the cathode. In small batteries such as those used in cell phones, laptops, and other portable electronics, this hazard while important to avoid does not typically create life threatening situations. However, in automobiles where the batteries will be on the order of 10,000 times larger, a fire in such a large battery can be very big, and very difficult to put out, and hence deadly to occupants of the car. This severe safety hazard is compounded, of course, when it is considered that fire inducing collisions occur often with other cars. If this would occur in a chain reaction of many lithium ion powered cars, the result could be catastrophic. Hence, there is a very critical need to replace flammable liquid electrolytes with inflammable solid electrolytes to dramatically improve the safety of batteries.

Furthermore, lithium ion batteries operate at more than 10 times lower energy density than theoretically possible (~300 mAh/gram compared to ~4,000 mAh/gram), because higher capacity metallic lithium anodes deposit lithium on recharging the battery in a dendritic manner than a planar manner. Such dendrites become dislodged from the metallic lithium anode and are no longer available for use in the battery and the capacity of battery rapidly decreases on repeated lithium loss at the anode due to the formation of dendrites. A more serious problem, however, is that these metallic lithium dendrites can puncture through the soft polymer separator used in the battery to mechanically separate the anode from the cathode and if this happens, the battery is

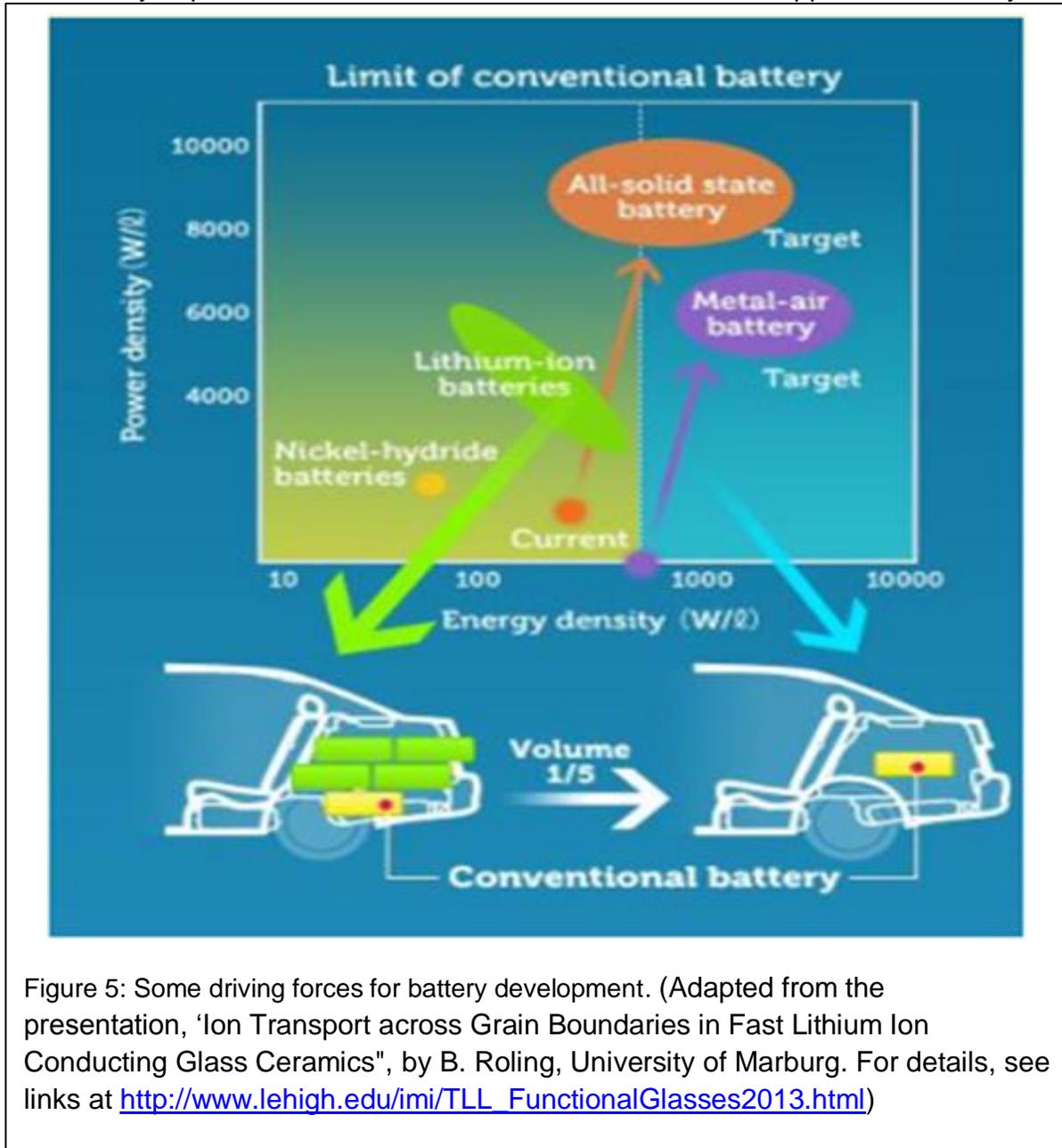


Figure 5: Some driving forces for battery development. (Adapted from the presentation, 'Ion Transport across Grain Boundaries in Fast Lithium Ion Conducting Glass Ceramics', by B. Roling, University of Marburg. For details, see links at http://www.lehigh.edu/imi/TLL_FunctionalGlasses2013.html)

short circuited and these dendritic filaments can heat up and ignite the organic liquid electrolyte.

For both of these reasons, researchers worldwide are looking for new solid electrolytes. In this context, glassy solid electrolytes have among the highest Li^+ ion conductivities of all materials. The wide compositional ranges, the low cost, ease of fabrication, the chemical and electrochemical durability, and the high ionic conductivities of glassy ion conductors make them a very promising solid electrolyte for use in new all-solid-state batteries. New compositions of glassy solid electrolytes, new studies of the grain boundaries that exist between glassy particles used in pressed compacted glassy solid electrolytes, and new glass-ceramic electrolytes are needed for using glasses in all-solid-state batteries in the future.

In summary, the conventional batteries are limited in energy density and power density, which creates problems for use in transportation systems where volume and weight are critical. For a more compact packaging in smaller energy storage devices, for example for cars, the separation of individual cells (as in conventional batteries) is not a preferred approach. Therefore, solid state batteries with reduced volume with multilayer structure are in the focus for compact packaging. The next-generation batteries need research in particular on the ion transport mechanism across grain boundaries in fast Lithium ion conducting glass-ceramics³.

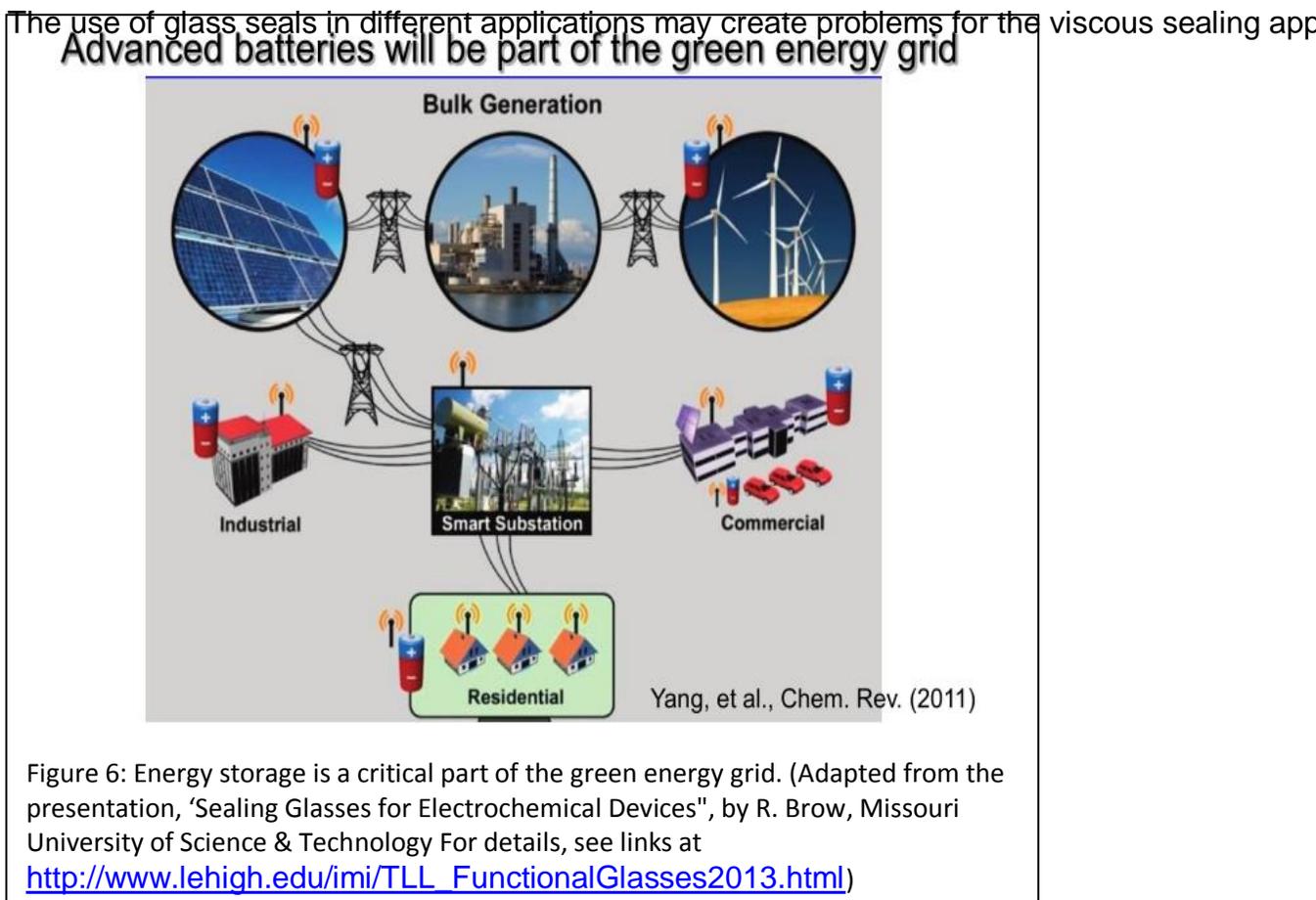
Bernhard Roling (University of Marburg, Germany) reviewed **“Ion transport across grain boundaries in fast lithium ion conducting glass-ceramics”**. Fast lithium ion conducting glass-ceramics are promising materials for all-solid-state lithium batteries and for lithium/air batteries⁴. In these materials, crystalline grains with e.g. NASICON, garnet or perovskite structure exhibit lithium ion conductivities up to 10^{-3} S/cm. However, grain boundary resistance often limits the total conductivity of the material. Very little is known about the nature of this grain boundary resistance. By combining broadband electrochemical impedance spectroscopy with high-resolution TEM, it was shown that there are materials in which the grain boundary resistance is caused by purely geometrical current constriction due to small grain contact areas, while in other materials, the grain boundary transport is characterized by a higher activation energy than the grain transport⁵⁶. In order to learn more about the nature of the higher activation barrier, nonlinear impedance measurements were carried out on the grain boundaries using high AC electric fields, which allow considerably higher fields exceeding the DC breakdown strength without significant deterioration of the samples. The results were compared to nonlinear current-voltage measurements on the grain boundaries of oxide ion conductors, where space charge layers often introduce additional activation barriers⁷.

In solid-state Li-S-batteries with $\text{Li}_2\text{S-P}_2\text{S}_5$ glass as electrolyte the charge transport is strongly determined by the formation of the interfaces. The interface between solid electrolyte and cathode materials is a critical part and protective coatings are used to manipulate the device performance. The open crystalline structure of NASICON, garnet or perovskite is most favorable for fast Li ion conductors and they are candidates for all-solid-state lithium batteries and for lithium/air batteries. The theoretical energy density of Li-air batteries is comparable to mechanical energy from 1 kg gasoline.

The total conductivity is limited by the grain boundary resistances. Different models have been used to describe the ion transport across the grain boundary interface (brick layer model, nano-grain composite model, finite element calculation for not perfect contact of the grains areas, space charge model). The results for the two investigated model materials can be summarized as follows.

- In $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) grain and grain boundary resistance exhibit the same activation energy. Purely geometrical current constrictions exist; the fraction of contact area is about 25%. The results can be explained by LAGP grain boundaries.
- For the commercially available Ohara glass-ceramic ($\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ doped with other oxides) grain boundary resistance exhibits a slightly higher activation energy than the grain resistance. The grain boundary resistance is not caused by a single (space charge) barrier, but by several serial barriers. The thickness of the grain boundaries is in the range 5-10 nm. Amorphous phases and high degree of crystallinity coexist in grain boundaries.

Richard Brow (Missouri University of Science and Technology, USA) evaluated **“Sealing glasses for electrochemical devices”**. He noted that hermetic seals are used to isolate reactive components in many electrochemical systems and oxide glasses are often the materials of choice for various applications because they offer a wide range of engineering possibilities for the design of such devices. Glasses can be processed in many ways (screen-printing, tape-casting, solid and sintered preforms, etc.) to accommodate different seal designs. They can form strong chemical bonds with different types of materials used in a hermetic package such as metals and oxides. The thermo-mechanical properties (coefficient of thermal expansion and sealing temperature (viscosity)) of a glass can be tailored for compatibility with a wide variety of packaging materials. An added advantage for many glass-forming systems is that an operational seal can be formed from solid glass, a solid glass-ceramic, and for some high temperature solid oxide fuel cell (SOFC) designs from a viscous liquid, thus expanding the range of sealing applications. In addition, certain glass chemistries can be utilized that are chemically compatible with other materials in the electrochemical system. For example, borate glasses are much more stable in contact with lithium metal than are silicate glasses, and so are the material of choice for seals in many Li-battery designs. These and other examples of glasses used in the design of lithium-batteries, sodium-batteries, and SOFC's were reviewed, and the need for new glass compositions with enhanced performance characteristics for emerging electrochemical devices were discussed. The following issues were especially examined: the interfacial reactions that occur when glasses are sealed to various materials; glass crystallization kinetics - in regards to both the formation of glass-ceramic sealing materials and the stability of a viscous SOFC seal; and long-term stability both at high temperatures (like those encountered in an SOFC) and in the presence of reactive electrolytes (like those used in Li- and Na-batteries).



increased basicity. In addition, one must consider that the gas permeability is higher in the metastable liquid than in the glass.

There is a lack of data on the thermomechanical parameters (viscosity, expansion, etc. as a function of temperature) for multi-component sealing glasses, which can create up-scaling problems. It also makes the application of finite-element simulations difficult for different geometrical approaches (stacks systems). At present alternative glasses are still lead-bearing low T_g glasses, which have some stability issues.

Currently, the field of sealing glasses offers many opportunities to explore new compositions. It provides an excellent materials science platform. Studies of topics like chemically stable non-silicate compositions, crystallization around the liquidus temperature or high temperature compatibility with metals need to be carried out in greater detail. Glass seals will be the enabling materials for many technologies in the future, e.g. for reliable Li-batteries or biomedical devices. But optimization is still required for Na/S, Na/NiCl₂ and SOFC systems. Requirements and key element to use sealing glasses in the production of future more advanced high tech products are:

- the ability to model the sealing processes
- accurate viscoelastic property data
- well-controlled manufacturing process parameters
- well-understood 'application' conditions

Steve Martin (Iowa State University, USA) reported on “**Glass for energy storage: advancing the energy density and safety of batteries**”. The need for higher energy and power density batteries is growing worldwide. However, at the same time,

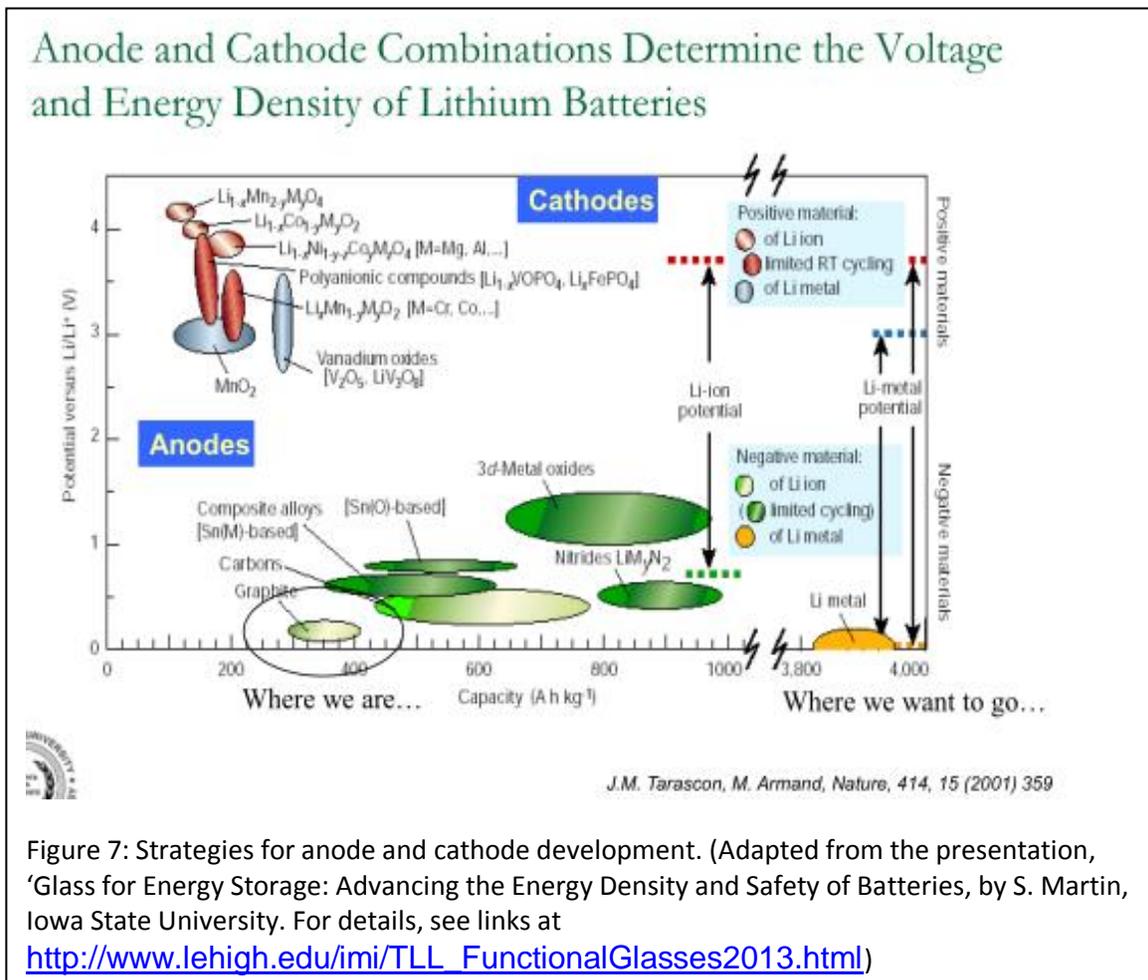


Figure 7: Strategies for anode and cathode development. (Adapted from the presentation, ‘Glass for Energy Storage: Advancing the Energy Density and Safety of Batteries, by S. Martin, Iowa State University. For details, see links at http://www.lehigh.edu/imi/TLL_FunctionalGlasses2013.html)

these next generation batteries must be safer, lower cost, utilize more earth abundant materials, and be manufactured using greener technologies. The worldwide ubiquitous use of portable electronics and their increasing demands for energy and power in smartphones, laptop computers, tablet computers, cordless power tools, and a myriad of other portable electronic devices in use today has exploded the demand for higher energy and power density batteries, but at the same time there is expectation to lower the cost, increase the safety, and incorporate “green” manufacturing and recyclability. Concurrently, the rapid increase in the worldwide production of CO₂ due to the combustion of fossil fuels has accelerated the interest in electrifying transportation systems by converging the electrical grid with cars and trucks. Such a convergence requires extreme energy and power density batteries that are well beyond the limits of current Li-ion battery technologies and chemistries. To achieve the required increase in energy and power densities while simultaneously increasing the safety, lowering the

cost, and greening their manufacturing requires entirely new approaches to battery chemistries, design, and materials.

One particularly promising strategy leads to the concept of all-solid-state lithium battery. Such solid state lithium batteries eliminate the need for capacity lowering carbonaceous cathodes, the use of flammable liquid electrolytes that foster metallic lithium dendrites, and the need for low capacity high mass transition metal oxide cathodes. By enabling the safe use of metallic lithium on the anode, the use of non-toxic, non-flammable solid electrolyte separators, and the use of air as the cathode, more than an order of magnitude increase in the energy and power density of lithium cells can be obtained. The core scientific and technological breakthrough enabling such all-solid-state lithium batteries is the development of new solid electrolytes - glassy solid electrolytes hold great promise as low cost, green, stable, and high Li^+ ion conductivity separators in next generation batteries.

A review of the current state of the art included carbon anode, liquid electrolyte, and transition metal cathode for lithium batteries, identifying the critical challenges with the use of this design to advance the energy and power density to the levels sought for the future. The current state of the art in new lithium battery chemistries and designs was summarized and the increases possible in energy and power densities of Lithium batteries described. Finally, a discussion was started on the development of new glass compositions that promise to resolve many of the challenges for the development of next generation lithium batteries.

By concentrating on the performance and safety aspects, solid state batteries appear attractive for which several glass compositions have been considered both as solid electrolyte and anode materials. In the last case, for example, an increased attention is placed on the development of new Li battery anode with higher storage capacity - comparable to unit activity of Li^0 , while maintaining safety. The determination of quantitative structure-properties relationships becomes fundamental to the future perspective on the limits of solid state battery performance. Key challenges for the future are:

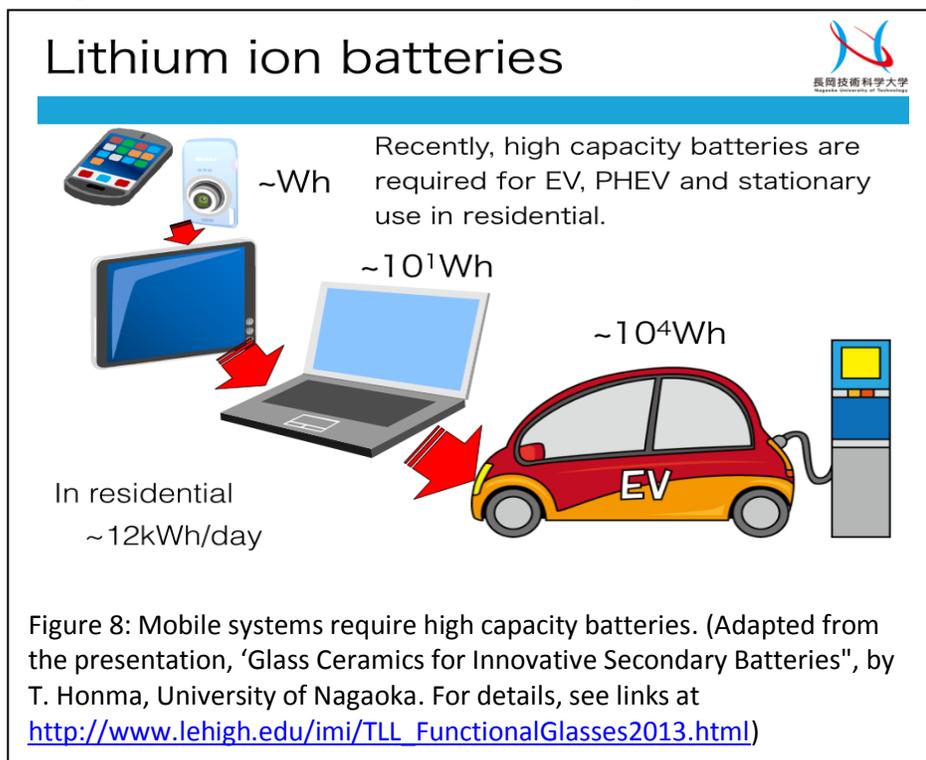
- design and optimization of the material, (for example, for solid electrolytes in solid state batteries the role of the matrix needs to be established),
- the limited conductivities of glasses investigated and
- the role of the migrating ion (Li^+ , Na^+)

For an effective improvement in optimization and design of specific compositions the role of short and intermediate range order structure should be understood. A new non-oxide glass system as solid electrolyte for new room temperature Na battery was suggested in which mechanical milling is used for amorphization of the mixtures of the starting materials. The conductivity and glass transition study of melt quenching and mechanical milling of $\text{Na}_2\text{S}+\text{P}_2\text{S}_5$ glasses, concluded that the two techniques lead to glasses with similar structure and properties. To increase performance and competitiveness of glass materials more economic but efficient cations such as Na^+ should be considered for incorporating into specific glass matrix.

Glass production methods play an important role in the industrialization of the final material. In addition, new functionalities for glass are proposed like Li^+ ion conducting chalcogenide glass anode, which conducts Li^+ rapidly to ensure fast

electrode kinetic and charge transfer, and also GeS_2 Li-glass based anode that shows much better reversibility in comparison to GeS_2 glass with Ge metal.

Tsuyoshi Honma (University of Nagaoka, Japan) presented a paper on “**Glass-ceramics for the innovative secondary batteries**” with focus on electrodes for Li batteries. LiFePO_4 is attracting much attention as a next-generation cathode material used in lithium-ion rechargeable batteries (LiBs) because of its high theoretical capacity of 170 mAh/g and high temperature stability owing to the highly covalent bonding between oxygen and phosphorus. Although the electronic conductivity and diffusion rate of lithium ions in LiFePO_4 are lower than in existing electrode materials, it can be used in LiBs in the form of a fine powder coated with an electron-conducting layer.



In general, LiFePO_4 is synthesized by a solid-state reaction or hydrothermal synthesis. However, the solid-state reaction requires a long time to control the chemical composition and size of LiFePO_4 particles. The hydrothermal synthesis provides products with higher purity at lower reaction temperatures, but controlling the particle size and reaction time is still difficult. By using crystallization process of glass materials, it is easier to control crystal morphology and size distribution from uniform glass matrix.

Unique techniques are proposed to fabricate phosphate based cathode materials prepared via crystallization of glass precursor. Precursor glass has very homogeneous composition, which permits the fabrication of, LiFePO_4 free from any detrimental intermetallic byproducts such as ferromagnetic Fe_2P , which works well even under the high current density condition⁸. The heat treatment of the mixtures of glass powders and glucose (5 wt%) at crystallization temperatures in a reducing atmosphere of H_2 -Ar forms olivine-type LiFePO_4 crystals covered with conductive carbon. The charge/discharge curves exhibit plateaus at 3.4 V.

But the battery package in an electrical vehicle (EV) must have capacity of over 10kWh. Accordingly, much lithium is required. Unfortunately, lithium resources are unevenly distributed in the world and lithium metal is classified as a rare-commodity. In the near future a rise in material cost is expected. Accordingly, other alkaline and alkaline earth ion based secondary batteries are proposed. In particular, sodium, being

just under lithium in the periodic table, appears attractive. It exhibits high redox voltage (2.7 V for Na/Na⁺) after lithium (3.03 V for Li/Li⁺). Some work has been reported focusing on cathode materials for this system. Typically, layered rock salt type α -NaCrO₂, which is an analog of LiCoO₂, is known as cathode active material for sodium ion battery. Although its layered rock salt exhibits good electronic conductivity and sodium ion intercalation the use of cobalt prohibits its utilization. Very recently a new cathode candidate Na₂FeP₂O₇ triclinic P1- crystal was fabricated by the glass-ceramics process⁹. The precursor glass, which had the same composition as Na₂FeP₂O₇, was prepared by the melt-quenching method. The glass-ceramic was obtained upon the heat treatment of precursor glass powder with 10% glucose addition as a reducing agent of Fe³⁺. In an electrochemical charge-discharge testing, Na₂FeP₂O₇ exhibited 2.9 V, 88m Ah/g, which is 90% for the theoretical capacity during 2.0-3.8 V cut-off voltages. Thus Na₂FeP₂O₇ glass-ceramics are promising, low-cost, safe cathode material for sodium ion battery.

The motivations for new battery materials are numerous, besides the desire for achieving higher energy densities (voltage x capacity in Wh) and high storage capacity (Ah). Other key aspects to be considered include enhanced cyclability, fast charging/discharging rates, no anisotropic volume change, safety, negligible deterioration of capacity, performance over a wide temperature range, short ion diffusion distances, no memory effects, long lifetime and low environmental impact. With these boundary conditions all the different components have to be optimized, i.e. cathode materials are needed which accept electrons from the external circuit through reduction reaction, and anodes which release electrons to the external circuit through oxidation reaction easily. The electrolyte should be an ion conducting material, with negligible electronic conduction, that provides a medium for fast ion transfer between cathode and anode, without participating in the electrochemical cell reaction. In addition, the cell voltage should be maximized, which is determined by the difference of chemical potential of the electrodes relative to the ions being transferred, i.e. the Fermi energies of anode and cathode have to be located within the band gap of the electrolyte. With all these expectations, LiFePO₄ is a good candidate cathode material – it does not evolve O₂ during heating, converts to electrochemically inert quartz structure and is less reactive with electrolytes, and seems to be useful in batteries for consumer electronics to automotive¹⁰. Another advantage is that different approaches are available to produce LiFePO₄, which are based on powders with controlled Fe²⁺/Fe³⁺ ratio (sol-gel, hydrothermal, solid-state reactions, coated with C, nanostructured) or glass-ceramics (crystallized from glass, various crystal products).

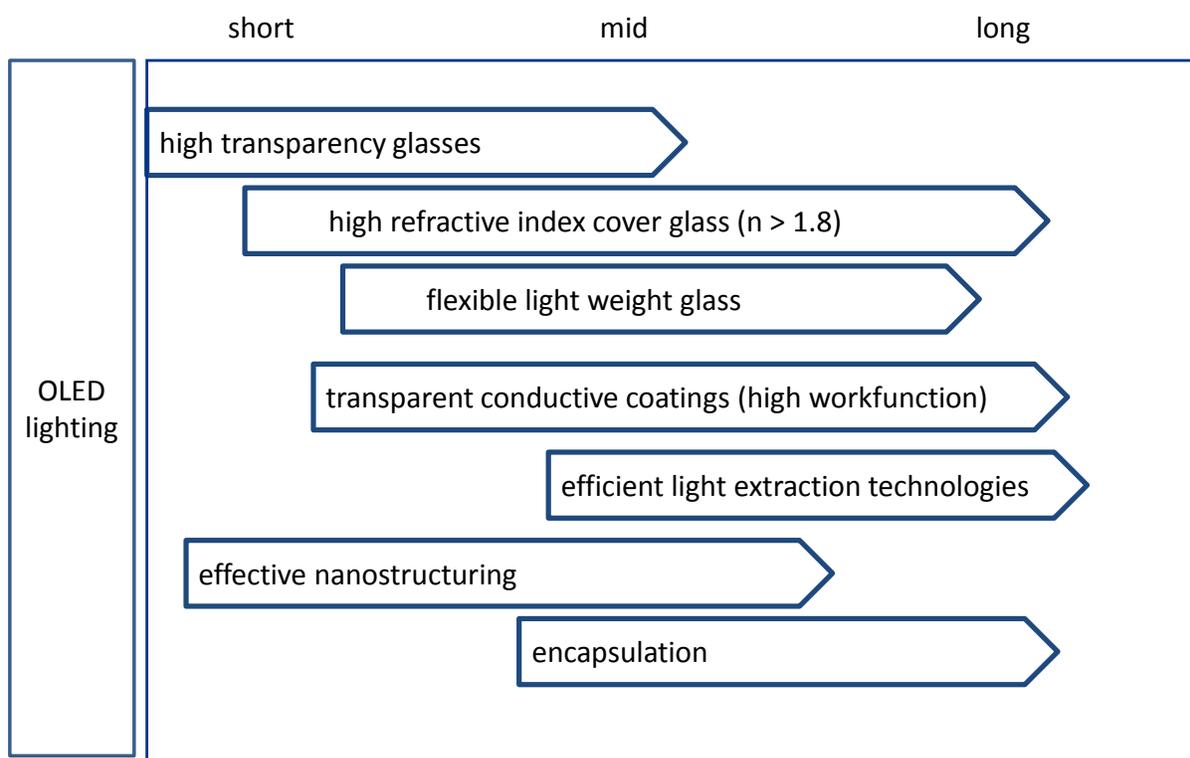
2.4 Summary: Glasses for Energy Technology

The usage of glass in energy technology has a long tradition. The first light emitting systems used the transparency of the material and the invention of the light bulb by Edison could not be realized without glass. Electricity distribution networks used glass fairly early as insulator. In the last decades photovoltaic created a prospering market for flat glass. Since the needs of the society has concentrated recently more on energy storage technologies, glass research has become more crucial with potential for making a big impact in this field.

Functional Glasses: Properties and Applications for Energy and Information

Several applications of glass in energy technologies were discussed during the conference. Glasses for the emerging field of **OLED lighting** were addressed first. Cost reduction is needed in this area, such as for low-cost high transparency glass and low-cost transparent conductive coatings with high work function (as anode). Future development activities should focus on high refractive index cover glass ($n > 1.8$), flexible light weight glass, efficient light extraction technologies and encapsulation. See Roadmap 1.

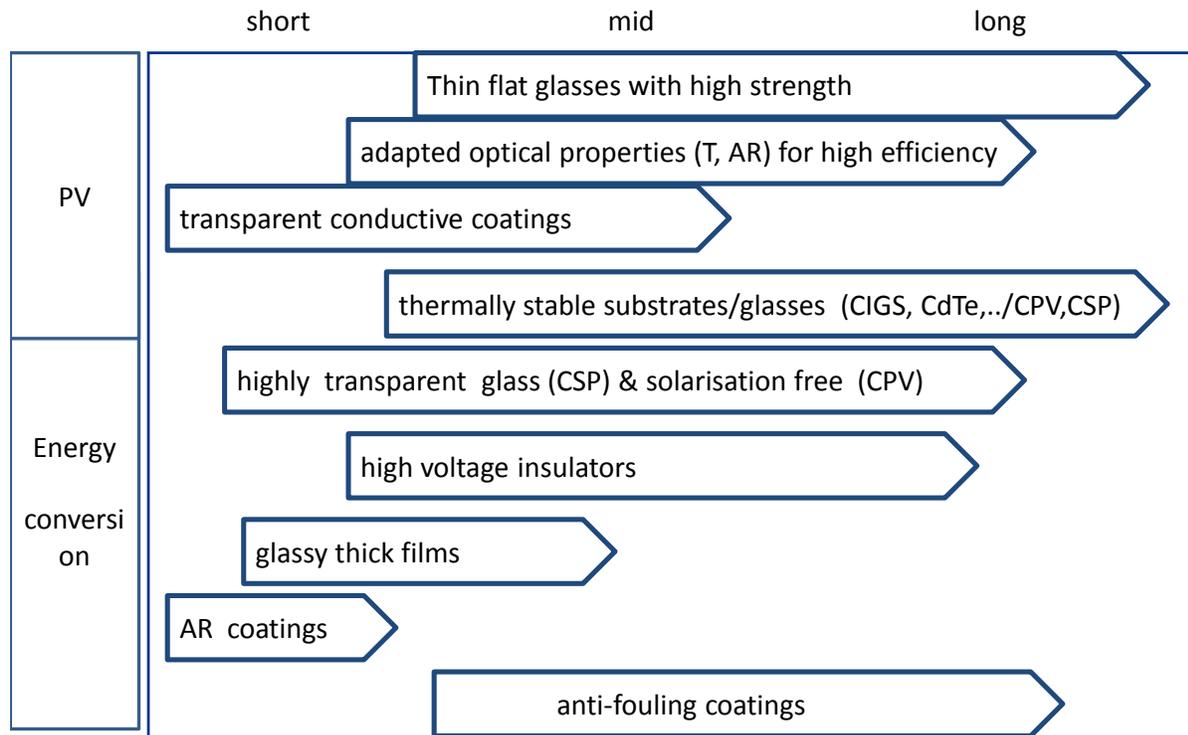
Roadmap 1. Applications in Energy Technology



Cost reduction measures play a prominent role also in **photovoltaic** devices, and glass is one of the main material cost factors. R&D activities for PV float glasses should concentrate on thinner glasses with higher strength to support the realization of thinner modules. For increasing light efficiency, we want optical properties like higher transmission and anti-reflecting surfaces, but also patterned surfaces, self-cleaning surfaces etc., which need to be studied in greater detail. Additionally, the electrical and optical properties of TCO should be improved. See Roadmap 2.

In **energy conversion** systems the alterations of glass surfaces and functional coatings are of high importance. Also the bulk properties of the materials may have to be improved for special applications. Highly transparent glass is needed especially for CSP, where the influence of Fe on the transmission has to be minimized. Thermally stable glass substrates (for CIGS, CdTe films, concentrated photovoltaics (CPV) and CSP) are desired and the materials should be solarisation free (particularly for CPV). The glass is gaining importance as high voltage insulators. Besides various coating functions like antireflective (AR) or anti-fouling, a high potential for glassy thick films was postulated for coal power plants, other fossil power applications and biomass-gas applications. See Roadmap 2.

Roadmap 2. Applications in Energy Technology

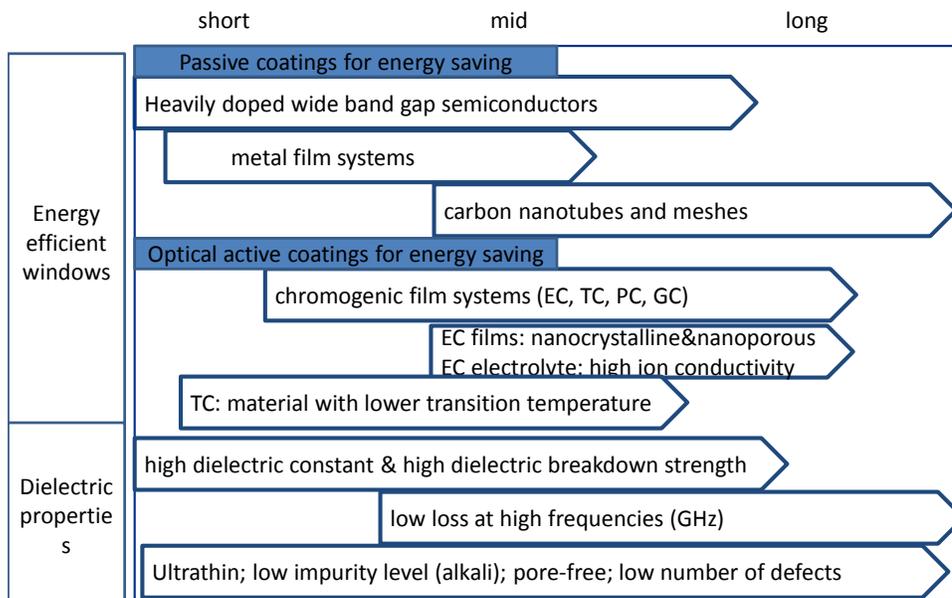


Functional Glasses: Properties and Applications for Energy and Information

Various favorable glass properties are identified for different applications in energy technology. In particular **energy saving** measures in buildings can be realized with cost effective glasses that also meet the environmental requirements. Classical window glass is the “weak link” in the energy consumption of buildings; the installation of energy efficient windows can improve the energy balance drastically. Low-e coatings on glass are a standard approach in this direction for decades. Nonetheless, the energy saving properties of passive coatings can be improved with heavily doped wide band-gap semiconductors, metal films and, in the long term, with carbon nanotubes and meshes. A different category of solutions employs optically active coatings with more complex materials and processes. Chromogenic film systems (i.e. electrochromic (EC), thermochromic (TC), photochromic (PC), gasochromic (GC)) are in general multilayer systems which switch their optical properties (T, R, A) depending on the amount of injected or ejected charge (EC), the temperature (TC), photons (PC) or gases (GC). For EC films further R&D is necessary on the nano-crystallinity and the nano-porosity of the active films, and for the EC electrolyte higher ion conductivities are needed for fast switching systems. For TC films, materials with lower transition temperature have to be developed. See Roadmap 3.

The current trends in electronic and the semiconductor industries indicate that the **dielectric properties** of the materials will become increasingly more important. Here ultrathin glasses with smaller thickness and lower impurity level (alkali) are needed, which should be free of pores and very homogeneous materials with low defect level. Additional R&D activities should focus on obtaining higher dielectric breakdown strength and lower dielectrics losses at high frequencies (GHz). Materials with higher dielectric constants are desired; ferroelectrics materials appeared attractive in this regard. See Roadmap 3.

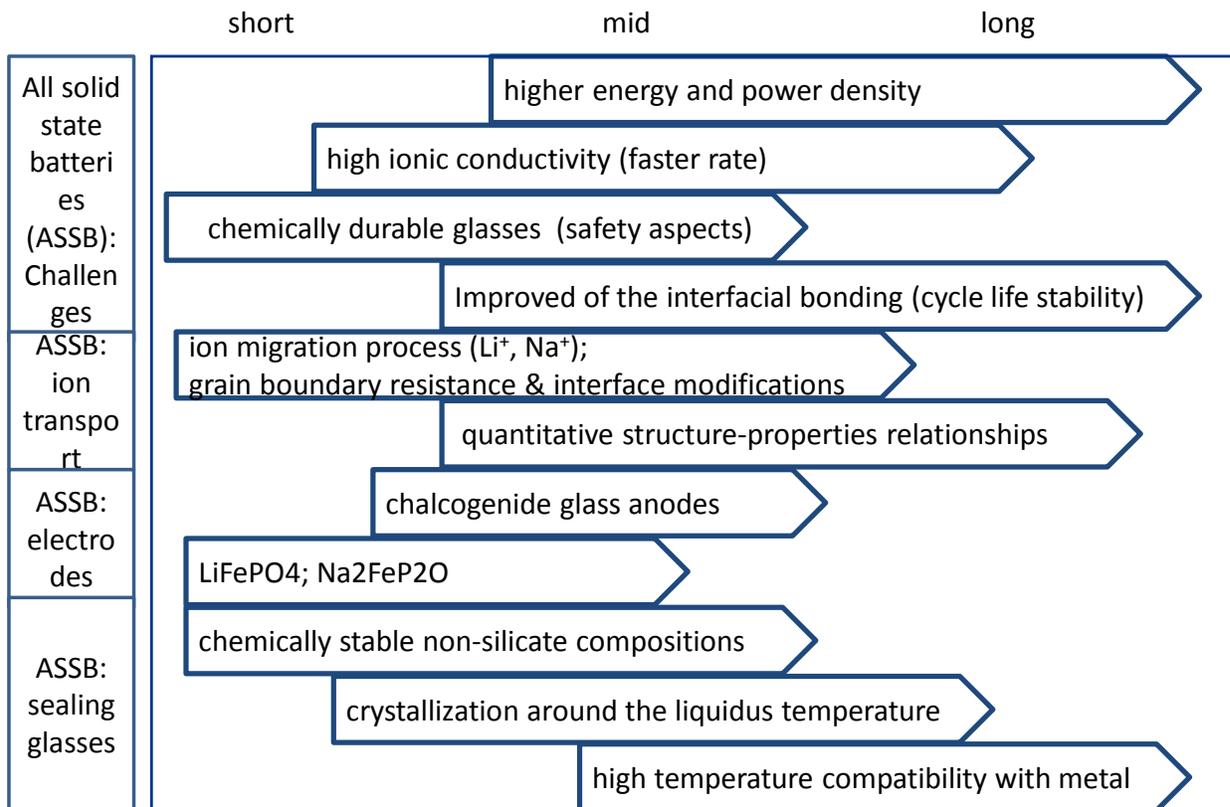
Roadmap 3. Properties for Energy Applications



Energy storage technologies gain in importance worldwide especially with the need of batteries for mobile communication systems. The critical R&D challenges related to all-solid- state batteries are: to develop materials for higher energy and power density batteries; higher ionic conductivities for faster rate batteries; more chemically durable glasses for safer, larger batteries; and to improve the interfacial bonding (anode and glassy solid electrolyte, and the cathode and the glassy solid electrolyte) to increase the cycle-life stability. A fundamental understanding of the (Li^+ , Na^+) ion migration and quantitative structure-property relationships of the materials is needed. Specifically, further research is needed on the influence of the grain boundary resistance and interface modifications on the ion transport in materials like lithium ion conducting glass-ceramics. Promising candidates for battery electrode materials are chalcogenide glass and LiFePO_4 and $\text{Na}_2\text{FeP}_2\text{O}$. See Roadmap 4.

The research on sealing glasses for batteries should focus on chemically stable, non-silicate compositions, especially on the crystallization around the liquidus temperature. All these materials must have a high-temperature compatibility with the metal in the structure. The sealing processes need to be improved and better understood with the help modeling tools. See Roadmap 4.

Roadmap 4. Energy Storage Technology



3. Glass in Information Technology

Changes in communication and exchange of information are some of the megatrends of the recent decades as fast developments and the progress in information technology has revolutionized our daily lives. The intrinsic material properties of glass had been the enabler for many displays, electronics and telecommunication applications in the past and seem to be attractive also for the future of these fields.

This chapter is divided in the sections on “Application of Glass in Information Technology” (Sec. 3.1) and “Glass Properties for Information Applications” (Sec. 3.2), ending with a summary in Sec. 3.3.

3.1 Application of Glass in Information Technology

The multifaceted usage of glass in information technologies is exemplified in this section with roll-to-roll thin flexible glass, microstructured optical fibers and TCOs.

Sean Garner (Corning Incorporated, USA) presented a talk titled “**Ultra-slim flexible glass for electronic applications**” and described in detail possible processes with roll-to-roll thin glass. He argued that since displays and electronics are becoming lighter, thinner, and more flexible, the choice of substrate continues to be critical to their overall optimization. The substrate directly affects improvements in the designs, materials, fabrication processes, and performance of advanced electronics.

With their inherent benefits such as surface quality, optical transmission, hermeticity, and thermal and dimensional stability, glass substrates enable high-quality, long-life devices. As substrate thickness is reduced below 200 μm , ultra-slim flexible glass continues to provide these inherent benefits to high-performance flexible electronics such as displays, touch sensors, photovoltaics, and lighting. In addition, the reduction in glass thickness also allows for new device designs and high-throughput, continuous manufacturing enabled by roll-to-roll processes. An overview of Corning® Willow™ Glass substrates was given, illustrating how they may enable flexible electronic device optimization. Specific focus was on flexible glass’ mechanical reliability. For this, a combination of substrate design and process optimizations has been demonstrated, which enable both sheet-based and roll-to-roll device fabrication on flexible glass. Demonstrations of roll-to-roll flexible glass processes such as vacuum deposition, photolithography, laser patterning, screen printing, slot die coating, and lamination were described. These basic capabilities enable continuous manufacturing of high-quality devices on flexible glass substrates.

The intrinsic glass properties make it attractive for future display and electronic applications, but transfer and adaption are needed for the roll-to-roll techniques and processes designed for polymer to glass. The development of edge-sealing techniques

Flexible Glass Sheets

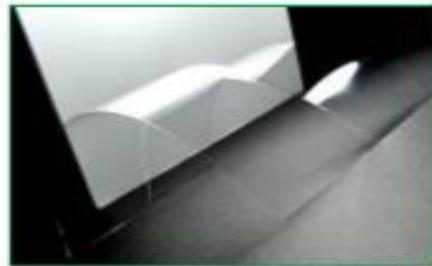
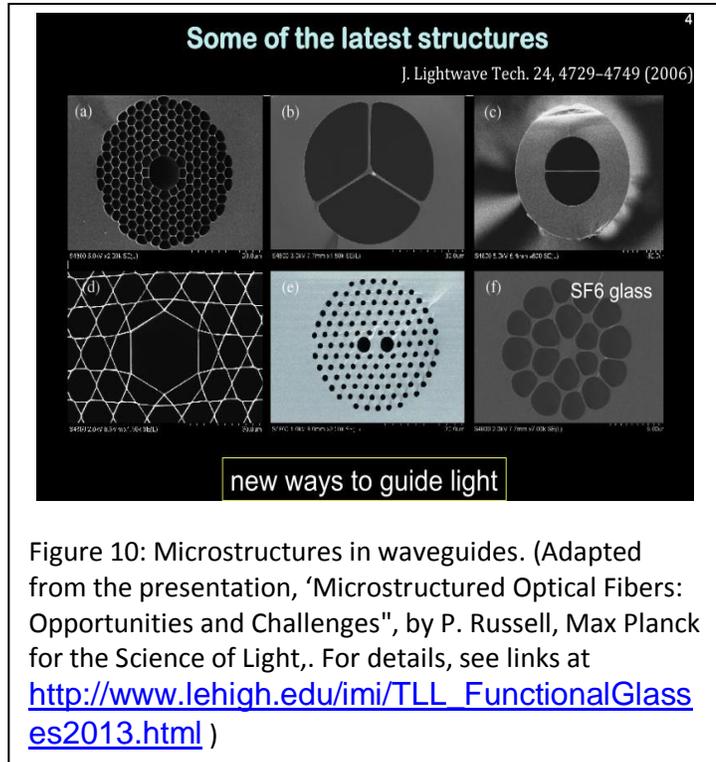


Figure 9: Bendable glass for R2R- processes. (Adapted from the presentation, ‘Ultra-Slim Glass for Electronic Applications’, S. Garner, Corning. For details, see links at http://www.lehigh.edu/imi/TLL_FunctionalGlasses2013.html)

was named as one technological hurdle to fully utilize the hermetic properties of glass. A broad technology spectrum seems to be applicable to the flexible glass, but details for surface treatments to optimize glasses for different deposition technologies were not described. In short terms, the most critical scientific questions concern the strength that dominates the potential applications at the moment, but as glass becomes thinner, the influence of surfaces would become greater. Then a better understanding of the nature of surfaces will become crucial. Important for future applications is the requirement of the handling thin sheets, i.e. the questions like what controls the strength of glass and how to protect glass from strength limiting damage will become very relevant.

Philip Russell, Max Planck Institute, Germany spoke on **“Microstructured optical fibers: opportunities and challenges”** and described how the past two decades have witnessed the emergence of glass fibers with intricate transverse microstructures, often with nanoscale features. Their ability to guide and manipulate light in new ways has fundamentally changed the "realm of the possible" in fiber-based light-matter interactions and led to many novel applications. Although the first reports of optical fibers with a transverse microstructure date back to the beginnings of optical communications in the early 1970s (when rather crude early fibers consisted of hair-thin glass capillaries drawn from preform tubes containing one or more small capillaries¹¹), interest in microstructured fibers resurfaced in the early 1990s when it was suggested that a periodic array of hollow channels could create a two-dimensional photonic band gap and allow light to be guided with low loss in a hollow core¹². The first "photonic crystal fiber" (PCF) with a solid glass core emerged from the drawing tower in 1995, and fiber optics entered a new phase¹³. The large glass-air index contrast allowed control of dispersion and polarization state over a much wider range, as well as guidance in a hollow core. Developments since then have been dramatic, with many new discoveries at both the fundamental and applied science¹⁴. In 2001 a major breakthrough made it possible to generate broad-band supercontinuum light from low energy laser pulses in solid-core PCF¹⁵. These fiber-based supercontinuum sources are now commercially available, and indeed are a common attachment in top-of-the-range microscopes. Astonishingly high spectral power densities, exceeding 10's of mW per nm, can be achieved from the near-UV to the infrared (an incandescent lamp has poor brightness in the blue and yields only ~10 nW/nm). The physics of this spectral broadening



is now well understood, and in principle it should be possible to produce broadband supercontinua for applications in the important "finger-print" region from 2 to 20 μm .

At present the challenge is to find a suitable glass with the required window of transparency and drawing characteristics. Hollow core PCF offers a further opportunity: because it can be designed so that more than 99% of the guided mode field resides in the hollow regions, the effective transmission loss can be many times lower than that of the glass itself¹⁶. This means that even glasses with quite high intrinsic absorption can be interesting for fashioning low loss hollow core fiber – for example in the mid-IR. In the field of sensing there is interest in preparing the glass surfaces so that they are able to bond chemically to ionic liquids or other sensing layers. The technology of fiber drawing has remained essentially unchanged over the past four decades. In view of the current demand for fibers with exotic nano-scale transverse microstructures, there is a strong need to improve the technology of "nano-scale glass blowing & drawing" to allow more reproducibility and precision. A promising recent development is the melt-filling of hollow silica microchannels at high pressure with lower melting-point glasses such as chalcogenides, which do not react with the silica¹⁷. This technique seems poised to deliver bright supercontinuum sources in the infra-red, pumped by lasers at around 2 μm wavelength.

As the internet continues to grow, it is expected that the current transmission fibers will become inadequate in around 2020. In this direction several R&D efforts are underway for high capacity transmission. Most research is focused on:

- Photonic crystal fibers to realize ultra-wideband transmission.
- Space division multiplexing by using multicore fibers.
- Development of new generation of amplifiers for spectral bandwidth.

Also, microstructured fibers are considered as a promising solution. However, most of these technologies are still under development in several research laboratories. Some technological challenges are concerned with the:

- Know-how of splicing of microstructured fibers;
- Laser coupling in multicore fibers;
- Low losses in specific structure mainly for telecom applications;
- Development of multicore amplifiers with adequate gain.

Another issue is related to specific design of silica fibers (hollow fiber with negative curvature of the core wall). The silica hollow fiber allows the transmission at 3 micron with 34dB /km optical losses. It provides an exciting possibility for laser delivery in this region mainly the Er^{3+} doped fluoride fibers. Also, it will be possible to extend the transmission to the highest wavelength (4 - 5 micron) using such design of silica fibers. Special design of microstructured fibers is needed in a dual nanoweb fiber waveguide, where nonlinear phase change is observed as a result of optically induced mutual attraction between two guiding glass sheets. This structure is promising for the observation of optomechanically self-trapped guided beams. Twisted photonic crystal fibers represent an additional opportunity as a filter for specific wavelength. The filter effect observed is analogous to the whispering gallery phenomenon.

Potential future applications include:

- Lab-in fiber for using PCF as a microfluidic channel that guides light
- Optomechanics with hollow core PCF for laser manipulation of particles and cells

- Nonlinear optical devices to control ultrafast nonlinear optics in gases, e.g. tunable deep UV light
- Nanowire plasmonics devices based on nanowire arrays

In conclusion, with optical losses of such fibers being reduced beyond those in conventional fibres and with an understanding of the enormous potential offered by the new structures, fibre optic technology stands ready to be transformed. Soon, the microstructured fibers will cover several domains not only telecommunication, but also health, environment and energy. But progress and development work are needed for

- Hollow core PCF made from “soft” glass (e.g. high power delivery of IR radiation at 10 microns),
- New techniques for producing nanoscale glass fiber structure and
- Optical glasses with other properties, e.g. magneto-optical, UV transparent, low losses and higher refractive index.

Since Transparent Conductive Materials (TCM) on glasses are critically important for applications in information as well as energy technology, Driss Lamine (Saint Gobain, France) presented an overview titled “**A general introduction for the use and needs of TCMs in glass industry**”. The applications of TCM aim on heat preservation, sun management, safety, and comfort on one hand, and to meet the needs of transparent electrodes on the other hand. Various materials are used for the improvement of thermal insulation by glazing, which can be categorized in two main groups: transparent, oxide conductors (TCOs) and transparent coating conductors (TCC) based on metallic systems. Examples of TCOs include $\text{SnO}_2\text{:F}$, ZnO:Al , $\text{In}_2\text{O}_3\text{:SnO}_2$ (ITO), and that of TCC include Ag, Nb or Mo, embedded in an anti-reflective coating system. A broad spectrum of deposition techniques is used in the production of the coating system, which influences the respective film properties remarkably. Sometimes special post heat treatment is necessary to achieve higher conductivities. Modern triple glazed units with high solar factor can be more energy efficient than walls of houses. TCC low- e coatings with anti-condensation effect can be realized, which is important since condensation becomes an issue for high performance insulating glazing units.

The choice of transparent electrodes for active glazings is strongly dependent on the specific active system where they play different roles with prescribed characteristics. Thus, for example, electrodes for electrochromic devices (EC) have to be highly conductive, highly transparent (including in the near infrared) and chemically stable; here injection-ejection and collection of charge are the most relevant parameters. TCOs that are used as top electrode for PV-CIGS, need a high transparency in the absorption region of the absorber, a relatively good conductivity (to avoid ohmic drops) and a good durability; the choice of these coatings is mainly cost driven. In Liquid Crystal application polarization is the most important issue and the electrodes need only a moderate conductivity, but they have to be highly transparent (no haze) and chemically stable.

Finally, the functionalizing of glass surfaces with transparent conductive materials is crucial for the reduction of the CO_2 production since the consequent application may significantly reduce the energy consumption for heating or cooling for buildings.

3.2 Glass Properties for Information Applications

Various properties of glass are needed for applications in information technology. Besides the mechanical properties like scratch or damage resistance, optical properties like refractive index for wave guiding or the nonlinearity are exploited; sometimes modification of the material with laser light is of importance. The relevance of these topics in information technology is summarized and discussed in this section.

In the session on chemically strengthened glass with improved damage resistance, Tim Gross (Corning, USA) spoke on “**Sharp Contact Damage in Ion-Exchanged Cover Glass**”. The primary failure mode in chemically strengthened cover glass for portable electronic devices is from sharp contact damage, i.e. localized permanent deformation to the glass surface, which results in strength limiting median/radial cracks. The in-use sharp contact damage may be replicated using various techniques including diamond indentation and grit blast abrasion. The deformation response of ion-exchanged glass is highly dependent on both the contact geometry and rate of contact. Resistance to the formation of median/radial cracks increases as the contact angle becomes blunter and causes deformation with less shear and more densification, e.g. the quasi-static indentation threshold for median/radial cracking for Corning® Gorilla® Glass is 50-100 grams force (gf) when measured using a 120° indenter tip compared to 5000-7000 gf when measured using a 136° (Vickers) indenter tip. Comparing quasi-static to dynamic indentation, the faster rates appear to favor deformation by densification and may also result in higher crack initiation loads. In dynamic Vickers indentation experiments, the median/radial cracking threshold of Corning® Gorilla® Glass is ~60 kilograms force (kgf) at 400 mm/s loading. Contact damage evaluation experiments have been performed on Corning® Gorilla® Glass samples, which exhibit typical compression stress profile, i.e. compressive stress >700 MPa and depth of surface layer region of ~50 microns.

The excellent optical transparency combined with improved damage resistance by chemical tempering and the low manufacturing cost make glass the leading candidate for applications in mobile displays for cell phones and tablets. The future expectations for these applications are:

- improve cosmetic nature of scratches formed on chemically tempered glass i.e. reduce the amount of lateral crack generation
- improve edge toughness after cutting a tempered glass
- reduce friction at surface initiating fractures
- increase depth of compression layer (DOL) while minimizing tensile stress region in the bulk

With these improvements the display glass would have greater resistance to scratching and fewer tendencies for catastrophic failure from consumer use. A breakthrough for this type of application would be a display glass that has a frictionless surface (coating) with increased scratch resistance, high DOL with increased resistance to larger flaws, and high edge toughness after cutting. The last characteristic would allow greater protection when exposed to edge loading and thereby reduce the need for edge packaging and protection.

Thierry Cardinal (University of Bordeaux, France) spoke on “**Glass and glass-ceramic for nonlinear optics: fundamentals and applications**”. Transparent materials exhibiting Nonlinear Optical (NLO) properties are key to the development of functional optics (waveguides, gratings, data storage, etc.). In recent years, due to new

laser developments, there has been a resurgence of interest in exotic glass and glass ceramic compositions. These materials combine low cost of fabrication and good compatibility with silica based systems, which offer the opportunity for developing nonlinear structures in integrated optical devices. The topic of glass and glass-ceramic for nonlinear optics covers a wide range of effects and applications. The most studied and cited phenomena are fast intensity-dependent index, third harmonic generation, stimulated Raman, second harmonic generation and the multiphoton absorption. After several years of fundamental and applied research, the development of specific glass and glass-ceramic compositions exhibiting NLO properties is now reaching the stage of practical applications.

The Kerr effect, which is directly related to the third order nonlinearity, has been the subject of intense research since the 80's. Literature is available that describes the relationship between the Kerr effect (intensity-dependent index) and the composition or the glass structure. In a first approximation, the nonlinear optical response follows the polarizability of the anions. The main contribution of the glass network to the fast variation of index has been identified. For a complete description of the phenomenon, the glass structure has to be taken into account. Recent results have shown that the Kerr effect of unusual glass compositions is promising, for instance, for self-phase modulation and broadband light generation in the near infrared.

The third order nonlinearity in resonant mode is also of particular interest. Indeed, Raman amplification has undergone a revival due to the rapidly increasing bandwidth needs for information transmission, both for long haul and local area networks, and recent developments in the telecom fiber industry and diode laser technology. In contrast to rare earth doped fiber amplifiers, for which the range of wavelengths is fixed and limited, Raman gain bandwidths are larger and the operating wavelength is fixed only by the pump wavelength and the bandwidth of the Raman active medium. It has been demonstrated that the Kerr effect and Raman gain phenomena follow the polarizability of the material and are strongly affected by the local structure of the non-conventional glass compositions such as tellurites.

Second Order Nonlinearity (SONL) can be obtained in glass upon appropriate modification. Since this phenomenon is not naturally present in a centrosymmetric material, the creation of an axial symmetry under thermal poling is necessary to introduce SONL properties. It has been demonstrated that stable SONL can be achieved by controlling the mobile ion migration and the resulting embedded field.

Glass-ceramics have been also the subject of intense research for nonlinear optics. Here the main issue remains the transparency of the material. Second Harmonic Generation is the nonlinear optical effect that has been the most studied in glass-ceramics that take advantage of the glass matrix and the nonlinearity of non-centrosymmetric crystalline compounds. Glasses incorporating semiconductor or metallic nanoparticles are also of great interest for nonlinear optics. The fabrication of colored glasses with narrow band-gap is at the origin of a new interest in glass-ceramics that could be used as saturable absorbers in mode locked lasers in the near infrared. The field of glass and glass-ceramics for NLO properties remains a very active research area. The common interest of scientists of the academic and industrial world for unconventional material compositions is leading to new motivation for understanding both fundamentals and applied aspects.

“Simple” glasses are not enough for future applications in nonlinear optics. The desired material should have not only high nonlinear coefficients but also address the losses. For some of the material factors, which are holding back the maximization of nonlinear optical effects and for a greater improvement, a multi-partner collaboration is required among optical physicists, glass scientists, and optical engineers. Modeling can play a crucial role in advancing the use of nonlinear optics in glass. Structure modeling of intermediate range units - one of the grand challenges of glass currently - would also help understand the role of tellurite chains. The modeling of nonlinear optical behavior is the subject of ongoing research, but the role of structure modelling is still a challenge. The modelling tools can contribute to the improvement of the materials to increase THG and SHG by factors of 10^4 , which would be an exceptional success. More scientific investigations are needed to (a) clarify whether thermal poling is the best strategy for maximizing SHG, (b) to understand the role of structure, both at the short and intermediate ranges, and (c) to determine the potential of active crystallites or metallic nanoparticles with plasmon resonances in glass-ceramics, like LiNbO_3 in silicate glass ceramics.

In the session on Nanophotonics, Limin Tong (Zhejiang University, China) gave an overview on “**Microfiber and Nanofiber photonics**”. Optical microfibers and nanofibers (MNFs) are glass fibers with diameters close to or smaller than the wavelength of the guided light^{18,19}. Fabricated by top-down physical drawing of glass fibers or bulky glasses, MNFs have circular cross-section, uniform diameter, smooth surface and large length, which enable optical waveguiding with tight confinement, strong evanescent fields, abnormal waveguide dispersion and low optical losses¹⁹. Inspired by the great potential and curiosity of guiding light on a lower dimension, the research on optical MNFs has been attracting increasing attentions. A variety of research, ranging from theoretical designs and simulations, experimental fabrication and optical properties to photonic applications has been reported. As summarized in the “MNF tree”²⁰ the research on MNFs, may be categorized into five areas based on the underlying optics (waveguide and near-field optics, nonlinear optics, quantum and atom optics, plasmonics, and optomechanics), which has brought numerous opportunities in renewing and expanding the fiber optics and technology on micro/nanoscale.

Specifically in the areas of waveguide and near-field optics, and plasmonics, numerous photonic applications can be realized e.g. in the first area micro-coupler, tiny Mach-Zehnder interferometer, micro resonator, micro/microfiber dye laser, micro filters, ultra-compact microfiber Bragg gratings and microfiber optical sensors with high sensitivity and compactness (including microfiber-microfluidic optical sensors). The potential applications in the area of plasmonics include Mach-Zehnder interferometer and hybrid “Photon-Plasmon” circuits and devices with applications as sensors and modulators.

In general, glass micro and nanofibers offer favorable properties for manipulating light on the nanoscale. When incorporated with waveguide optics, near-field optics, nonlinear optics, plasmonics and optomechanics, these 1-D glass nanostructures may bring more new opportunities, both for fundamental research and technological applications. But further miniaturization of photonic devices is strongly dependent on the enhancement of optical nonlinear effects, and photonic engineering for light absorption, conversion and emission. Advances in nanofiber photonics will depend on improved

confinement and transport of light, while the improvements in nanowire optics will need a better understanding of nonlinear and quantum optics of atomic wires, and waveguide and near-field optics of microwires

The interaction of laser with glass was explained by Jianrong Qiu (South China University of Technology, China) with a presentation on “**Femtosecond laser micro-processing of glass: fundamentals and applications**”. Laser-induced modification and damage in transparent materials have attracted considerable interest and stimulated studies since the advent of high power pulsed lasers²¹. The availability of laser pulses with femtosecond duration allows materials to be subjected to higher light intensity than ever before, opening the door to the study of laser/material interactions in a new regime^{22,23}. Tight focusing of ultrashort (~100 fs) infrared laser pulses of moderate energy (typically 1–10 μJ) into a glass results in very high, localized (in space and time) intensities, in excess of 10^{14} W/cm². There are unique advantages in favor of fs laser micromachining of transparent materials over other photonic-device fabrication techniques. First, the nonlinear nature of the absorption confines any induced changes to the focal volume. This spatial confinement combined with laser-beam scanning or sample translation makes it possible to micromachine geometrically complex structures in three dimensions. Secondly, the absorption process is essentially independent of the material, enabling fabrication of optical devices in compound substrates of different materials. Thirdly, during irradiation the fs laser pulses deposit large amounts of energy into the glass through nonlinear multiphoton absorption, and heat accumulation occurs at high repetition rates as new pulses arrive before the energy of previous pulses is fully dissipated, causing an increase in temperature around the focal point. Based on these efforts, various femtosecond laser induced microstructures have been observed in the past decades, such as the formation of color center, micro-void and refractive index change, valence state change of doped ions, precipitation of nanoparticles, formation of single-crystal architecture, etc. Promising applications for the fabrication of various micro-optical devices have also been demonstrated. The recent R&D on fs laser induced unique phenomena were discussed, including polarization-dependent nanograting, non-reciprocal writing, periodic void array along the propagation direction of the laser beam, elemental redistribution etc. Finally, future research directions were suggested.

The spatial and temporal high-intensity profiles provided by focused fs laser and the resulting spatial selectivity of the laser-induced modification in glass provide the basis for a new category of products in which the various types of micro-modifications are induced in glass, e.g. laser-induced refractive index changes, valence changes, crystallization, formation of nanocrystals and nanogratings, etc. Potential applications include optical memories, waveguides, various passive optical devices such as gratings and Fresnel lenses, surface nano-structuring for solar cells, etc. Glasses are a uniquely suitable material for fs laser modification, because of its isotropy, homogeneity, compositional and doping flexibility, and formability into complex shapes. Using pulse shaping one may realize quantum coherent control of excited states in glass; that will become a new important research direction of the fs laser interaction with glass. Most of the potential applications have not been commercialized yet primarily because of the challenges remaining with the scaling of the process to mass production. Another great challenge is still the reproducibility and control of device parameters, related to the

fact that the resulting modification depends sensitively on laser parameters, such as pulse duration, pulse energy, repetition rate, polarization as well as focusing conditions and materials composition. More studies are needed on the temperature effects during fs laser processing, and differences between low rep rate (1 KHz) and high rep rate (MHz) lasers and on the questions dealing with the depth dependence of fs laser modification and effects of self-focusing. Since 3D rewritable optical memory, the fabrication of 3D optical circuits, the 3D micro-hole drilling, and 3D precipitation of functional crystals had been experimentally demonstrated, the additional findings of further investigations will pave the way for the fabrication of functional micro-optical elements and integrated optical circuits.

Yong Gyu Choi (Korea Aerospace University, Korea) spoke on “**Phase-change**

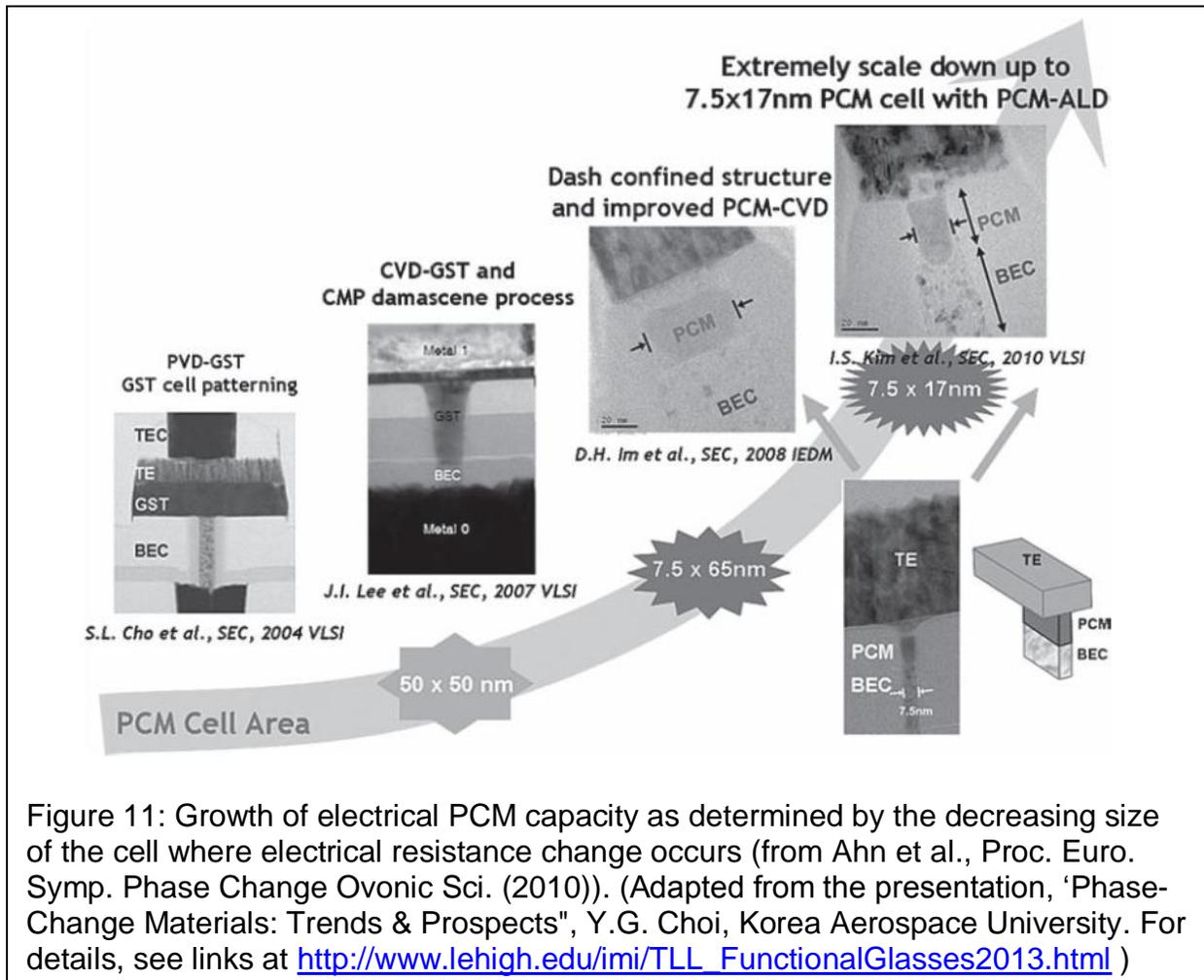


Figure 11: Growth of electrical PCM capacity as determined by the decreasing size of the cell where electrical resistance change occurs (from Ahn et al., Proc. Euro. Symp. Phase Change Ovonic Sci. (2010)). (Adapted from the presentation, ‘Phase-Change Materials: Trends & Prospects’, Y.G. Choi, Korea Aerospace University. For details, see links at http://www.lehigh.edu/imi/TLL_FunctionalGlasses2013.html)

memory (PCM) for information storage”. At present, information is stored mainly in two kinds of memories: dynamic random access memory (DRAM), and non-volatile flash memory (using NOR or NAND logic gates). DRAMs have the shortest write/erase time of <10 ns, but also short retention time (tens of ms). Flash memories can store information for >10 years, but require longer time to write/erase (μ s to ms). PCMs are attempting to combine both of these attributes of very fast write/erase time (10s of ns) and long retention period (>10 yr).

Chalcogenide glasses have enabled competitive technologies for storing and retrieving information. For example, the current technology for information storage on rewritable CDs and DVDs is based on a unique combination of the very fast glass \leftrightarrow crystal phase change by a laser pulse and corresponding change in optical reflectivity exhibited by certain chalcogenide compositions. The same phase-change can be accomplished with an electrical pulse, in which case the information is stored in the significant difference between the electrical resistances of the two phases. This electrical PCM is hailed as the latest revolution in information storage, as described in Fig. 11.²⁴ A serious commercial effort for making phase change random access memory (PRAM) started in 1999, and by early 2012 Samsung delivered laboratory level 8 GB device, and at the end of the year Micron offered 1 GB memory for mobile phones. In the case of optical PCM, the density of memory is limited by the optics (e.g. the wavelength), whereas for electrical PCM, cell design, film fabrication, and choice of material are important.

A PCM material should exhibit: high speed phase-transition (10s of ns), long thermal stability of the amorphous phase (10s of years at room temperature), large difference in reflectivity/resistance of the two phases, large number of operation cycles (>100K), and high chemical durability under ambient.²⁵ In addition, the following material parameters are important: crystallization temperature (T_x), melting temperature (T_m), threshold voltage, thermal conductivity in the two phases, and melt-quenching speed.²⁶ Considering the current needs, Choi prioritized these material requirements to the following three items: (a) Phase transformation time (particularly the crystallization time) should be shorter than hundreds of nanoseconds for high-speed mobile applications, and even shorter than tens of nanoseconds for dynamic random access memory (DRAM) applications. (b) T_x should be 150-200 C, so that the device is stable in automobile applications, while $T_m = 500-1000$ C so that the material can be melted with a Joule heat at a low electric power. The properties of surrounding dielectrics and electrode materials should not be affected by Joule heating for melting. (c) Phase change should be reproducible over 10^5 cycles with no significant change in material's composition - a requirement for nonvolatile memory.

There are three principal classes of chalcogenide compositions that have been identified so far for PCM: pseudo-binary GeTe-Sb₂Te₃, which show large contrast in electrical resistance as well as optical reflectance; Ag/In doped Sb₂Te (AIST); and Ge_xSb_(1-x). Interestingly, in the crystalline state, the first two compositions exist in cubic or distorted rocksalt structure, and the latter in hexagonal structure. Also, chemically they exhibit resonant bonding, which is the cause of their higher optical contrast. This type of bonding requires a longer-range order than in the conventional electron pair bond dictated by the 8-N rule. In the amorphous state, the structure seems to revert to a simple 8-N rule structure. Thus there is significant reorganization of the local structure as the material undergoes phase change.

In short, serious efforts are underway for replacing the DRAM and flash memories by electrical PCM. To achieve this goal, it will be necessary to obtain faster switching speed and longer retention time than allowed with the present devices. Also, the following additional challenges must be overcome:

Functional Glasses: Properties and Applications for Energy and Information

- The programming current density in the active volume ($>10^7$ A/cm²) is too high. It needs to be lowered, hopefully to the level of typical transistor or diode (10^5 - 10^6 A/cm²).
- The contact between the hot phase-change region and the adjacent dielectric can be a problem, if the melting temperature of the selected composition is too high.
- There is a fundamental tradeoff between the stability of the amorphous phase and the speed of phase change.
- There is an undesirable drift of the long-term resistance and threshold voltage.
- A detailed understanding of the electrical switching phenomena is lacking, especially the threshold switching.
- Designing and fabrication of phase-change films need to be developed, which will permit multi-level cell performance.

In the session on processing-performance of integrated optic structures Raman Kashyap (University of Montreal, Canada) spoke on “**Photosensitivity of optical materials for photonics and integrated optics**”. The role of photonics in everyday life has changed dramatically over the past decades. The availability of “ultra-low optical loss”, gorilla, electronically interactive, nonlinear and other glasses have made possible a plethora of applications. Several investigations focus on studying materials for integrated optics waveguides and devices, techniques for fabrication and processing as well as structuring of dielectrics for enhanced functionality. Ultimately, material properties limit functionality; however, these bounds have not yet been fully explored nor elucidated. Understanding the limits of photosensitivity through laser-material interaction is necessary to address the complexity of devices, which may become feasible in the future. Some questions remain: What limits the induced loss in UV-laser written waveguides? How can this be ameliorated? What processes can we use to alter properties to enhance their characteristics? Does structural change in dielectrics need be detrimental to optical properties? How much does serendipity play in determining performance? Can one make “perfect” ultra-long optical filters? A worldwide research is progressing on optical fiber, glass waveguides, materials photonics applications, periodically poled nonlinear optical materials and waveguides. The Fabulas laboratory is providing an unprecedented capability for processing large wafers up to 30cm in diameter, meter long optical fibers to investigate their photosensitivity and for the creation of new devices with the help of numerous lasers, including fs-CW at uv-IR wavelengths. Also the use of ablation and femtosecond lasers to structure glasses and nonlinear materials for novel applications is possible.

At an early stage many activities in this field were conducted on polymeric systems but today glass is considered as the best material in terms of homogeneity, loss and laser threshold. Thus glass will remain the best candidate in terms of potential improvements. The main trends which influence the product development in the future are materials engineering and development of new materials. The main requirements on the glass properties and the processability related to fibers are: the capability to control the uniformity of the core diameter to achieve an index variation of the core region to less than 10^{-6}); and an index change of about 0.1 - 0.2 which will have a huge impact for nanophotonics. Additional scientific challenges are the understanding of the femtosecond interaction process, and the formation of oxygen in voids. That is, what is

the role of the oxygen in general in the laser process and for laser cooling. The passivation of the surface of quantum dots is also a main issue. Technology-wise the fiber drawing process for fiber grating is important and a better understanding of the interface quality between the core and the cladding to improve the core size homogeneity is needed. The most critical scientific issues are related to: losses induced by structural changes; the effect of temperature during fs laser interaction and the role of the physical chemistry around the oxygen and of the mechanical stresses; the achievement of core shell semiconductor in glass for laser cooling; the realization of an index variation up to 0.2; the development of materials for infrared regarding volume Bragg grating transparent above 2 microns. For a further breakthrough in this complex field more interdisciplinary work is needed involving materials engineering (engineering, purity and homogeneity), materials synthesis, physics and optical engineering.

The recent status of research on fiber lasers was presented by Younes Messaddeq (University of Laval, Canada) in a talk titled “**Towards the development of advanced optical fibers**”. The tremendous growth of the Internet, and the large increase in traffic have produced a need for a novel class of flexible components. To operate at high bit rates beyond 150 Gb/s, optical communication systems will have to process signals entirely in the optical domain, in order to overcome the speed limitations associated with opto-electronic conversion. All-optical signal processing means a control of light by light, which is possible only in a nonlinear optical material. Furthermore, a trend in telecommunication networks has emerged over the past 30 years utilizing wavelengths that are progressively getting longer (from 0.85 μm to 1.3 μm and then to 1.5 μm) so as to minimize propagation losses. On this basis, we can envision that as new materials and new components (e.g. lasers) are developed, this trend will continue toward the middle infrared. Consequently, meeting the future challenges of the next generation of telecommunication systems will therefore require not only a better understanding of nonlinear optical processes, but also a parallel development of new optical materials. It is therefore time to revisit optical fiber design.

Developing multicore and multimode fibers for spatial division multiplexing represents actually one of the issues under exploration by several research groups. Simultaneously, optical routing and processing technologies must be researched to increase network efficiency and switch throughput. Developing optical fibers with enhanced nonlinear effects and electro-optic properties for optical processing represents another topic for development. The long-term solutions to the capacity limit of optical communication systems will be based on innovations in optical materials, waveguides and devices. Another area of recent development is microstructured fiber, which has multiplied the available degrees of freedom for the optical fiber designer. Much progress in this field has been achieved with the advent of highly nonlinear silica-based and chalcogenide glass fibers. Furthermore, glass fibers can be combined with polymers, metal coatings, electrodes or nanoparticles to enhance their responses. All these fibers represent a new generation of so called multifunctional fibers. Their impact on various fields of application such as environmental monitoring, biomedical devices and security/defense was reported in this presentation.

In particular, the changing requirements coming from the fast growing Internet demand a better understanding of nonlinear optical processes, but also development of new optical materials and devices to meet the challenges of the next generation of

telecommunication systems. The current focus is on the improvement of optical fibers, fiber lasers and fiber sensors, but further R&D is needed on topics like fs laser directed writing of optical waveguide in chalcogenide glasses, formation of nanograting on the surface, Raman fiber laser, fiber sensors and microstructured fibers. Fiber lasers are considered as the next generation of solid state laser, and fiber sensors have received much attention in recent years. Some of the emerging challenges are with the development of low-loss fibers for transmission at mid-infrared wavelength, mid-infrared lasers, and high power lasers for various applications. Chalcogenide glasses and fluoride glasses are the main candidates, but their chemical durability and photostability must be assured with a proper choice of composition. Chalcogenide glass fibers are considered as suitable for the generation of MIR super continuum. Nano-composite chalcogenide glasses containing Cr-ZnSe have shown potential for MIR laser, which indicates an important direction for the development of novel fiber lasers.

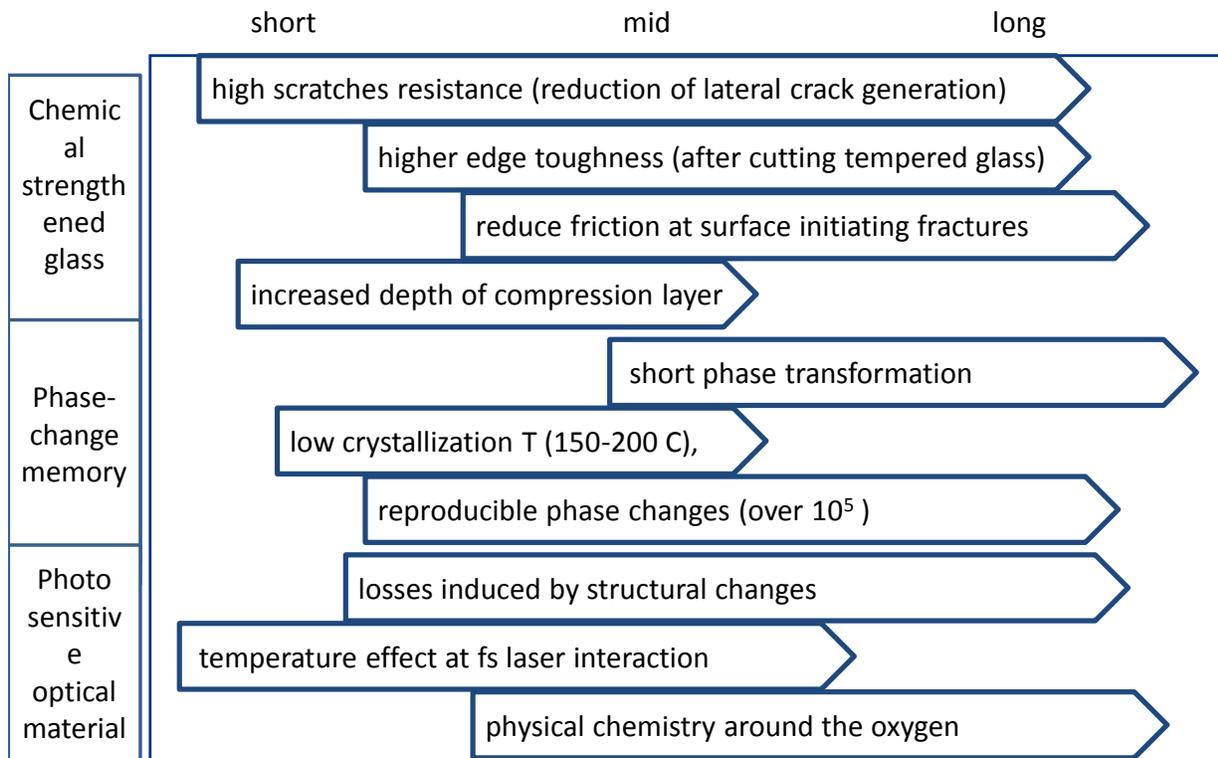
3.3 Summary: Glass in Information Technology

Glasses are the enabling materials of many products in information technology – although they are often not visible in the final products. For example, glasses are used for a long time for heat conservation, sun management, safety and comfort. With suitable coatings and transparent electrodes glass provides the main interface with the users of LCDs, PV, OLED or EC devices. More importantly, glass is also the enabler for many potential future applications. Flexible glass can be used in roll-to-roll processes for applications in high-performance flexible electronics, displays, touch sensors, photovoltaics, or OLED lighting. Microstructured optical fibers have the potential for enabling lab-in-fiber where PCF provides microfluidic channels that guide light. They are also needed in optomechanics with hollow core for laser manipulation of particles and cells; in nonlinear optical devices to control ultrafast nonlinear optics in gases, e.g. tunable deep UV light; or in nanowire plasmonics devices based on nanowire arrays. Micro and nanofiber photonic systems can be used in micro-coupler, Mach-Zehnder interferometer, micro resonator, micro lasers and microfiber dye laser, micro filters, ultra-compact microfiber Bragg gratings, microfiber optical sensors with high sensitivity and compactness, microfiber-microfluidic optical sensors, hybrid “photon-plasmon” circuits and devices with applications as sensors and modulators. Furthermore, fs laser micro-processing of glasses can help develop applications like optical memories, waveguides, passive optical devices (gratings and Fresnel lenses), surface nano-structuring for solar cells, 3D micro-optical elements and integrated optical circuits. Notwithstanding, several technological challenges exist for the realization of these different types of applications. For example, to obtain roll-to-roll processable thin glasses, problems like edge-sealing and handling of sheets have to be solved. For microstructured optical fibers, alternative technologies have to be developed for splicing of microstructured fibers and laser coupling with multicore fibers, or to achieve low losses in specific structures and multicore amplifiers with adequate gain for telecom applications.

For the different categories of IT products very different properties are needed. Some properties are very specific and have to be developed and adapted to the respective product specification. That is, the R&D activities can be useful for multiple applications or be designed for a singular application. For example, mobile information

systems (tablets, smart phones) need surfaces with high scratch-resistance (reduction of lateral crack generation) and reduced friction against surface initiating fractures, i.e. chemically strengthened glass with high edge toughness (after cutting tempered glass) but with an increased depth of compression layer (while minimizing tensile stress region in the bulk). In contrast, the material requirements for phase-change memory applications are fast phase transformation, low crystallization T (150-200 C) and reproducibility during phase change cycles ($> 10^5$). On the other hand, the critical scientific topics for the photosensitivity of optical materials for photonics and integrated optics are related to losses induced by structural changes, the effect of temperature during femtosecond laser interaction or the physical chemistry around the oxygen. In addition, the role of mechanical stresses is an issue in these materials; realization of refractive index variation up to 0.2 is needed; and materials are needed for the infrared volume Bragg grating that operates above 2 micron wavelength. See Roadmap 5.

Roadmap 5. Properties for Information Applications

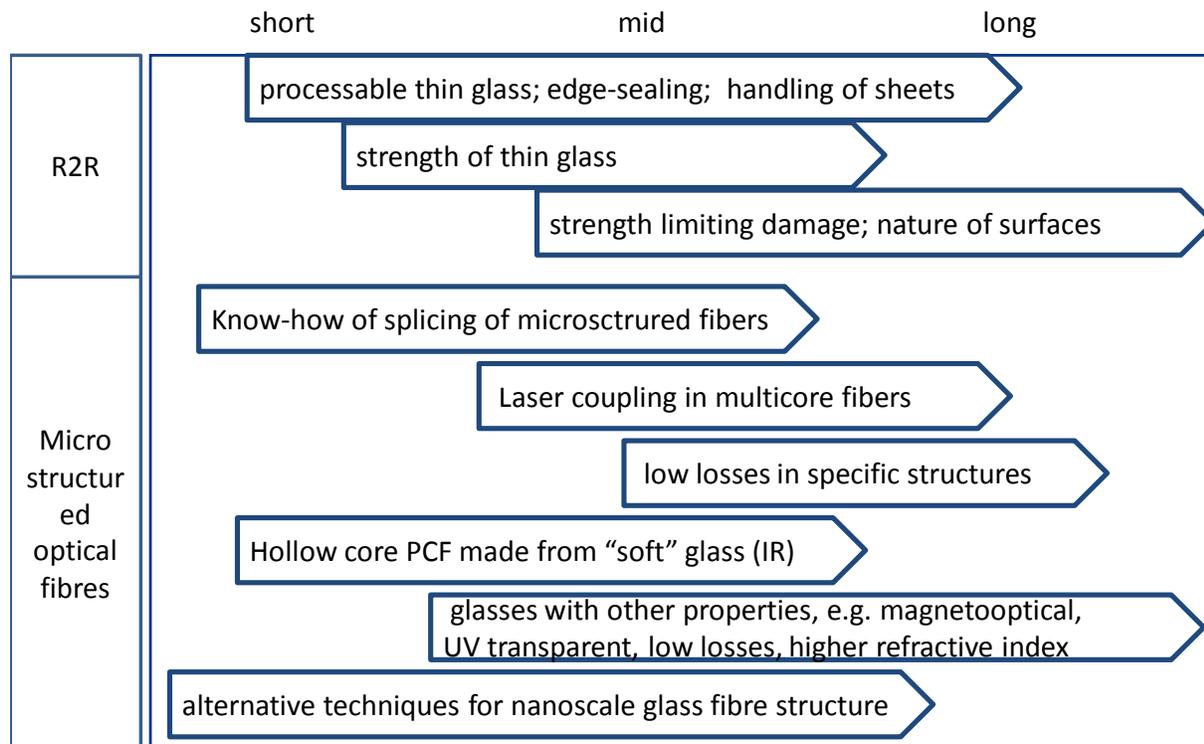


Functional Glasses: Properties and Applications for Energy and Information

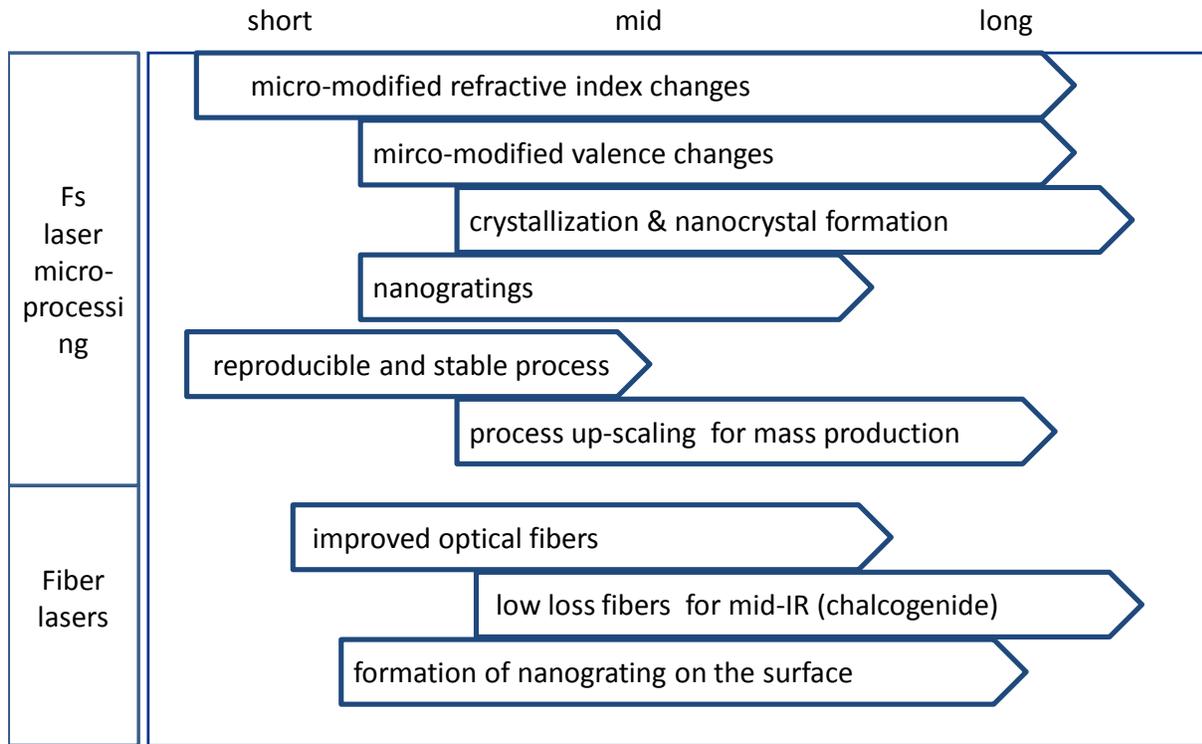
The R&D for processable roll-to-roll glasses has to focus on the strength of thin glass, on the strength limiting damage which is strongly related to the nature of surfaces. The activities on microstructured optical fibers should concentrate in the future on topics like hollow core PCF made from “soft” glass (e.g. for the high power delivery of IR radiation at 10 microns), new techniques for producing nanoscale glass fiber structure and optical glasses with other properties, e.g. magneto-optical, UV transparent, low loss, high refractive index, etc. To realize the progress of fiber lasers and fiber sensors, the R&D activities have to be primarily directed on the improvement of the quality of optical fibers, but also on formation of nanograting (on the surface) and microstructured fibers. See Roadmap 6.

Femtosecond laser micro-processing can be used, in principle, to induce micro-modifications, local refractive index changes, local valence changes and crystallization, nanocrystal formation and nanogratings. However, there remain major challenges before fs laser processing can be used routinely. More effort is needed to obtain a better reproducibility and a more accurate control of device parameters before an up-scaling of the process to mass production is possible. These are very difficult and complicated tasks because all material modifications depend sensitively on laser parameters (pulse duration, pulse energy, repetition rate, and polarization, focusing conditions). See Roadmap 7.

Roadmap 6. Applications in Information Technology



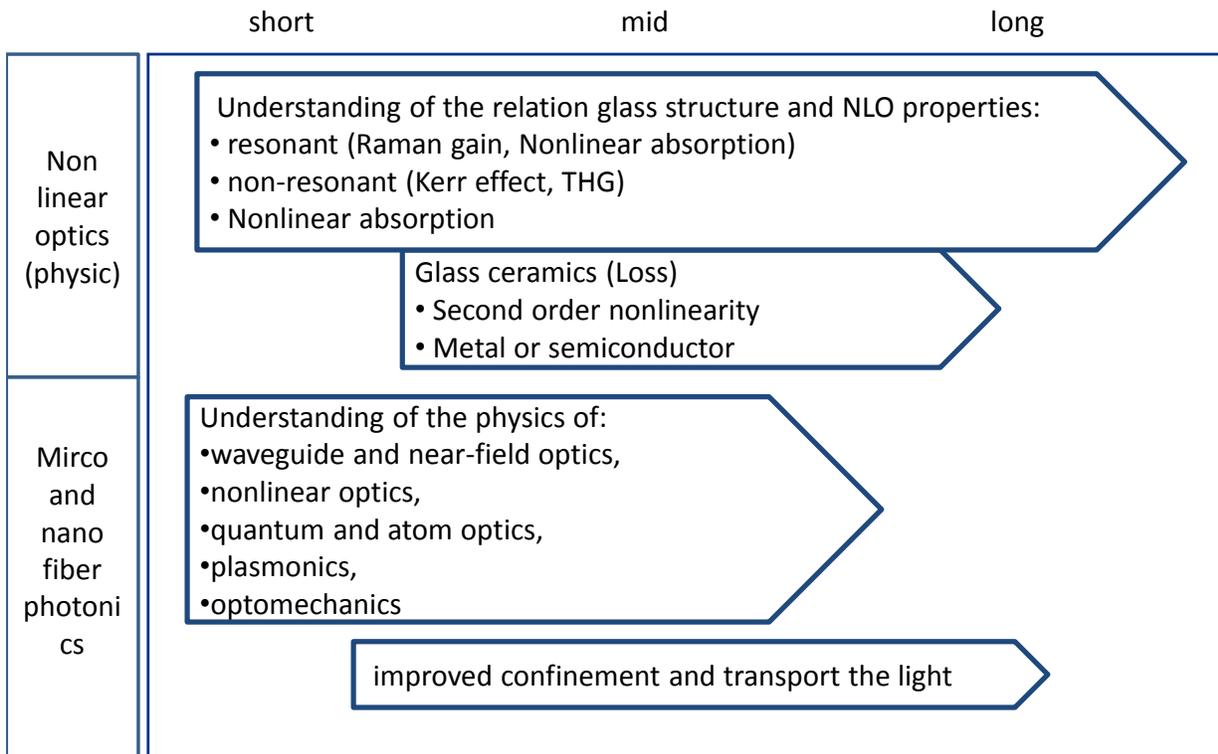
Roadmap 7. Properties in Information Applications



Functional Glasses: Properties and Applications for Energy and Information

The physics behind nonlinear optics and micro and nanofiber photonics is fairly complex and a better understanding of the relation between the glass structure and NLO properties is needed. Modeling tools can contribute much, but more detailed investigations of the resonant (Raman gain, nonlinear absorption) and non-resonant (Kerr effect, THG) effects, and nonlinear absorption have to be carried out. Second order nonlinearity of glass-ceramics (loss issues) will enhance scientific interest also in metals or semiconductors within glass. Third order and second order nonlinearity of materials will need an understanding and control of local phase separation or local crystallization. Advances in micro and nanofiber photonics will depend on improved confinement and transport of light. The improvements of nanowire optics will depend on a better understanding of nonlinear optics and quantum optics of atomic wires, and waveguide optics and near-field optics of microwires. See Roadmap 8.

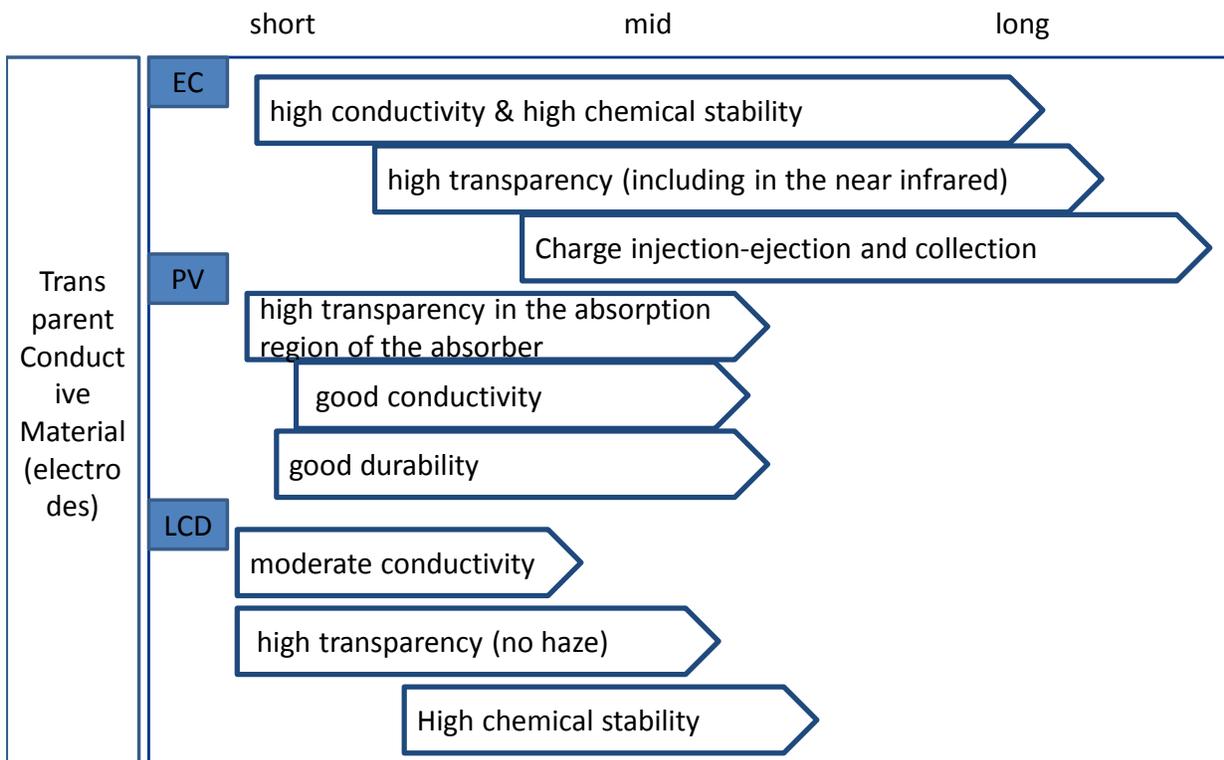
Roadmap 8. Properties for Information Applications



Functional Glasses: Properties and Applications for Energy and Information

Transparent conductive material (TCM) thin films on glasses are standard in many information technology devices, but the desired properties of the films are strongly dependent on the specific application. For EC systems the TCM must be highly conductive (because a high sheet resistance creates a potential drop which leads to inhomogeneous coloration), highly transparent (including in the near infrared), chemically very stable and provide rapid injection-ejection and collection of charge. TCM as PV top electrode should have high transparency in the absorption region of the absorber, have relatively good conductivity (to avoid ohmic drops) and a good durability. TCM for LCD need only a moderate conductivity, but a high transparency in the visible range (no haze) and be most chemically stable. TCM for OLED lighting should be on a low cost high transparency glass, and transparent conductive coatings should have a high workfunction because the film acts as the anode of the device. See Roadmap 9.

Roadmap 9. Applications in Information Technology



4. Glass Processing and Fabrication

In comparison to the topics in previous chapters that directly focused on energy and information technologies, rather different topics are considered in this chapter, which concern broader areas of processing and fabrication. Besides the continuing interest in increasing the energy efficiency in glass melting, glass surface damage during fabrication is evaluated along with optical element and large area device fabrication.

The session on glass melting was started by Roland Langfeld (SCHOTT AG, Germany) with a talk titled “**Making glass better**”. He summarized and reviewed critically the results of two following expert meetings which took place recently:

- As part of the ICG (International Commission on Glass) roadmap process for glass, in 2008 an experts' workshop was organized in Brigg, Switzerland focusing on glass production. It led to the requirements for a path towards lower energy consumption in glass melting as described elsewhere²⁷.
- In Nov, 2012 the ICG and SCHOTT held a one day workshop at Mainz, Germany with the participation of glass experts from Belgium, Germany, Japan, The Netherlands, Czech Republic and Turkey. Through a full day panel on "Energy Reduction in Glass Melting", they revisited the roadmap published by ICG ("Making Glass Better")²⁷, and assessed the progress made in the short and long term. The results related to energy saving in glass melting was presented and discussed.

Since 50 to more than 80 % of the energy consumption for glass production is related to the glass melting process itself, within the last decades glass industry has made significant progress to reduce the specific energy consumption. It is important to note that although 50 - 80% of energy is consumed in melting, much of the remaining part (i.e. 20 - 50%) is consumed in "post-melting" processes. Apparently, the state-of-art is significantly farther away from theoretical limit of these processes than in the case of melting. That is, significant energy savings may be realized more readily from post-melting operations than in the melting alone.

At the beginning the main driver was cost reduction and strengthening the competitiveness. Although these drivers are still of highest importance, additional pressure is building from environmental and climate control requirements. In some areas further decrease of specific energy consumption has slowed down due to technical or economic boundaries. On the other hand, legislation is putting more pressure on the glass industry to achieve even more demanding, sustainable energy savings and reductions in CO₂-output.

The following main topics were noted there:

- user reports on many incremental improvements in energy saving leading to significant energy savings in total
- improvements in simulation tools and sensors
- new insights in physical/chemical understanding of batch melting and (re-)fining as main source for energy savings
- progress made in new energy saving technologies like TCR (thermo chemical recuperation) and HOTOX (hot oxy fuel)
- intense discussion of the status of the segmented melter concept

Functional Glasses: Properties and Applications for Energy and Information

- report on the actual status of the Japanese inflight-melting concept.

The specific requirements for specialty glass industry (compared to soda lime glass production) were described in greater detail, which are

- higher melting and refining temperatures
- refractory material limitations and cooling limitations
- slower reaction rates for melting and especially for refining
- significantly higher demands of glass quality in terms of homogeneity and freedom of solid inclusions and gaseous inclusions

The gap between the status today and the results necessary to face the energy challenge of the glass industry had been illuminated, including those arising from specialty glass industry requirements for pre-competitive R&D.

The reduction of energy consumption and CO₂ emission is still a very serious and important issue for glass industry in general and is strongly related to science and technology but also to the economy and sometimes politics. This issue can be somewhat different in each country, depending on the type of energy and its market. What makes this topic even more complicated is that most of the existing roadmaps do not have clear numerical targets for the future, in relation to energy savings in glass production. Clear goals and numerical target values are needed and have to be scheduled in a roadmap for energy saving in glass production, otherwise most discussions and actions remain futile toward saving energy and do not motivate the realization of energy reduction. Furthermore, the market trend, energy source, and political pressure, as well as the energy issues are strongly related to the expected quality of glass products. Usually, higher the expectation of quality the higher is the energy consumption. Also, quality depends on application area. The current roadmaps show only an overview of research directions, and key issues which should be addressed for reducing energy consumption.

It seems that energy consumption in the melting of soda-lime container glass is almost at the theoretical limit when optimized conditions are used, indicating that no further research is needed in this field anymore; other glasses and processes still have room for a reduction of energy consumption. Often a collaboration of university and industry is not sought, especially, in the sector of commercial glass melting, because this area is full of high level secrets. Also because researchers in academia may not know the complete process, they cannot contribute effectively to these issues. On the other hand, most academics are not very interested in conventional glass fields where there is almost no room to change the process. However, the specialty glass processing seems to be a relatively open field, where advanced glasses and advanced processes are possible and needed.

Further progress in the glass melting may be categorized as follows:

- Incremental changes: improvements are progressing now in glass industry and each company; however, it is not discussed in public.
- Radical new concepts: should be carried out by industry-university cooperation; new technologies need an open discussion on advantages and disadvantages
- New/changing boundary conditions: changes of the society and the market have to be monitored; relevant for developing a powerful schedule of energy reduction.

In summary:

- In some cases of soda-lime glass, the reduction of energy consumption is approaching to a theoretical limit by optimizing melting conditions; more energy saving will be realized by each company.
- In the field of advanced functional glasses, there is a higher potential for reduction of energy consumption and advanced process; new technology should be discussed with melting experts.
- One of the main challenges in glass industry is energy-saving technology, which is not attractive to academia or young professionals.
- The (specific) energy consumption should be balanced by "CO₂-saving potential" of glass articles. Instead of setting an energy saving target, a roadmap could focus on reduced CO₂-pay-back time of a system. This will draw a friendlier picture of glass.

Tayyab Suratwala (Lawrence Livermore National Lab, USA) reported on his research on "Surface interactions on glass optics during fabrication, post-processing & laser operation". The state of surface is known to be very important for the performance of glass in numerous applications where it interacts with the surrounding chemical environment. In the case of silica optics used for high fluence and high peak power lasers, the role of surface features and their mitigation on laser damage resistance has been studied extensively up to ~20 J/cm² (351nm, 3ns). (see, for example, Fig. 12). However, much less is known about the precursors and their modification of surface

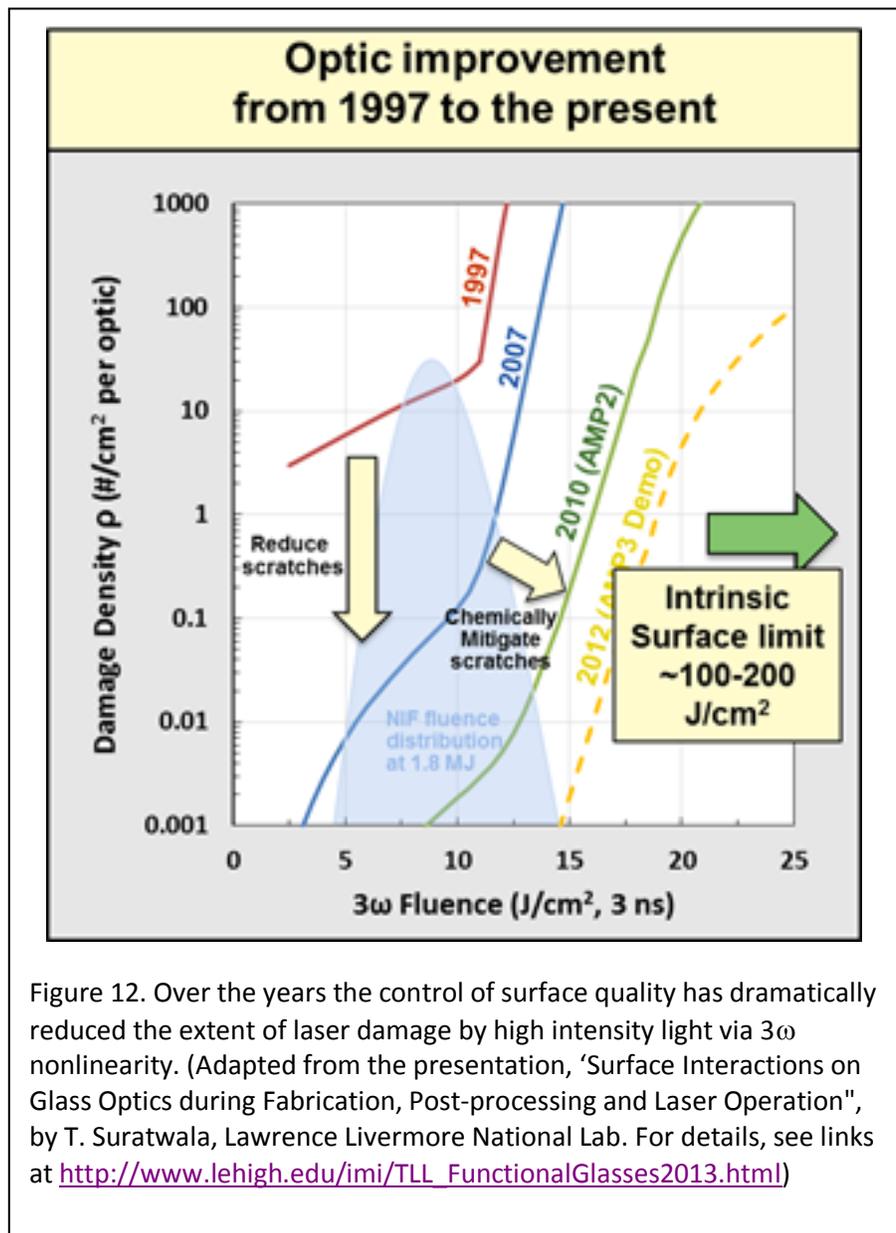


Figure 12. Over the years the control of surface quality has dramatically reduced the extent of laser damage by high intensity light via 3ω nonlinearity. (Adapted from the presentation, 'Surface Interactions on Glass Optics during Fabrication, Post-processing and Laser Operation', by T. Suratwala, Lawrence Livermore National Lab. For details, see links at http://www.lehigh.edu/imi/TLL_FunctionalGlasses2013.html)

by exposure to light at higher fluences approaching the intrinsic surface limit.. Indeed the quality of glass surface can limit the maximum peak power that can be available to the application of interest. The author has been investigating the precursors of laser damage to the glass, which are introduced during fabrication or subsequent handling. Some of the key precursors to laser damage include micro-scratches, micro-fractures, roughness, local topology variation, chemical and particulate contamination, etc., which may be introduced during commonly used finishing steps such as grinding, polishing, and lapping. This group has addressed laser damage of glass by understanding the changes that occur during optical fabrication where surface and subsurface damages occur during exposure to laser. They have developed several strategies to mitigate the damage using post-processing operations such as cleaning, chemical etching with HF-based acids, laser conditioning, and laser repair. To avoid debris, finishing of edges, where chipping would occur most likely, is recommended before the final polishing step. A novel buffered oxide etch process on fused silica optics and a laser conditioning process on borosilicate glass optics with multi-layer dielectric coatings have been shown to significantly improve the operating fluence of such optics. With this approach an improvement by more than four orders of magnitude has been accomplished since 1997 in damage density from 3ω irradiation. The current level of threshold fluence is still an order of magnitude worse than the so-called 'intrinsic' value of $\sim 200 \text{ J/cm}^2$ for glasses like silica (Note: the real threshold intrinsic to bonds and point defects in a material has not been established so far). Therefore, the target is to find ways of fabricating glass optical elements with this level of resistance to laser damage. To accomplish this goal we must develop a greater fundamental understanding of the source of laser damage at these very high fluences, the role of dangling bonds in the ultimate strength, and the intrinsic power handling capability of glasses.

The current effort related to optical fabrication has concentrated on understanding sub-surface damage management; forensics of surface fractures; higher fluence surface precursors; fundamentals of material removal; technology of full aperture & small tool optical finishing; low cost, precursor-free finishing techniques (called convergent polishing); dopant pair absorption and the development of high fluence optical filters; and combined CVD-laser surface treatment to locally repair optical surfaces. The future challenges are: deterministic finishing; science of finishing at microscopic and molecular levels including chemical interactions; and development of new finishing techniques.

The key topics related to laser exposure include: Mechanism of initiation and growth (precursors & modulation); precursor isolation and identification; quantitative understanding of initiation and growth of laser damage; understanding of solarization and modulation effects. For the future, one should be focusing on: higher fluence precursor identification and mitigation; understanding multi-pulse surface and radiation effects; understanding and mitigating debris-induced damage; understanding damage mechanisms on other glass optics (including coatings); and the development of new optical glass compositions such as high fluence optical filters.

With regard to finding practical solutions in the near term, three goals are identified: development of chemical/thermal-based flaw/damage mitigation; development of laser-based flaw/damage mitigation; and laser interference gratings development. The future directions should further include development of: new chemical

and laser mitigation strategies (e.g., for high fluence precursors, damage sites, conditioning); higher fluence multi-layer dielectric coatings; stable, high fluence AR coatings; and new materials for high fluence filters.

In the session on Optical Elements Fabrication, Xianghua Zhang (University of Rennes, France) discussed “**Production of chalcogenide glass optics: motivation, current status and future development**”. For introducing new functionality in glass, one often looks for new compositions with properties significantly different from typical oxide glasses. In this regard, chalcogenide glasses (ChG) stand out as the most promising class of non-silicate glasses, which exhibit unusual properties leading to novel applications but also challenges for manufacturing and performance in commercial devices. Compared to silicate glasses, ChG, especially selenides and tellurides are transparent to much longer wavelengths covering the two atmospheric windows at $\lambda = 3\text{-}5\ \mu\text{m}$ and $8\text{-}12\ \mu\text{m}$, which makes them immediately indispensable for applications in infrared (IR) optics. Note that the maximum intensity of blackbody radiation from objects at ambient temperature falls within $8\text{-}12\ \mu\text{m}$ window. At these wavelengths oxide glasses and silicon are opaque, so traditionally germanium single crystal or ZnSe has been the material of choice. In the past, the price of IR detectors was tens of thousands dollars, and the cost of Ge or ZnSe optical elements was a small fraction of total cost. The situation has changed dramatically in the last decade with the decrease in the cost of IR detectors. There is much pressure to produce low cost IR

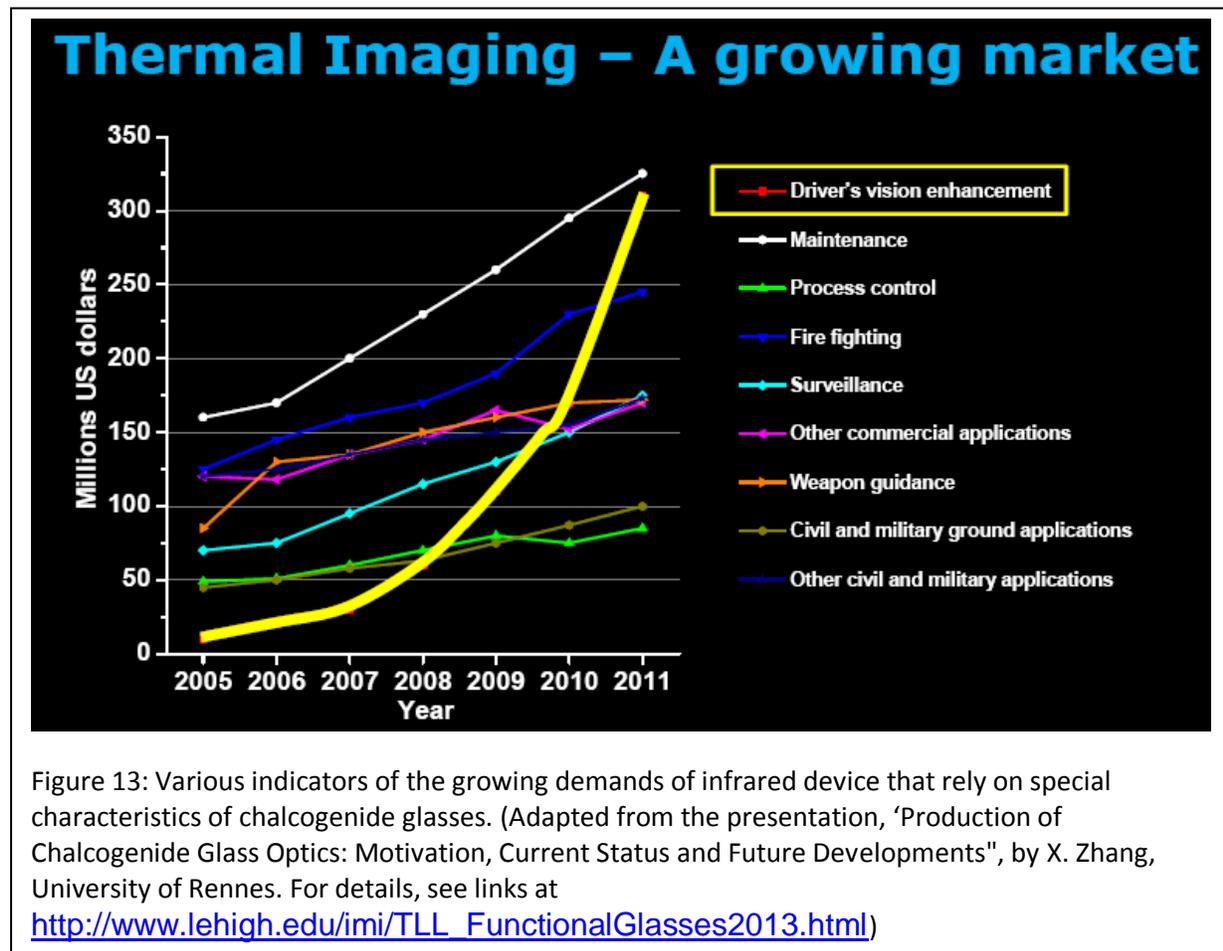


Figure 13: Various indicators of the growing demands of infrared device that rely on special characteristics of chalcogenide glasses. (Adapted from the presentation, ‘Production of Chalcogenide Glass Optics: Motivation, Current Status and Future Developments’, by X. Zhang, University of Rennes. For details, see links at http://www.lehigh.edu/imi/TLL_FunctionalGlasses2013.html)

optical elements, so that a range of new products can enter consumer market. Note that although many ChG are made of toxic elements, once they have combined chemically the glass itself is not toxic.

The presentation by Zhang focused on the fabrication of ChG optical elements for numerous applications such as in automobiles for driver's vision enhancement, maintenance and surveillance of operations, industrial process control, firefighting, thermal imaging, weapon guidance, civil and military ground applications, etc. An important advantage of ChG over Ge is their optical stability against temperature variation (dn/dT for the former is smaller by an order of magnitude lower.) Although the volume of glass needed for such applications is several orders of magnitude smaller than the current production of silicate glasses, a rapid expansion of its market is expected, especially with the development of relatively inexpensive uncooled focal plane array micro-detectors (see Fig. 13).

The successful penetration of a product in commercial market depends on the ability of its large scale production. It is in this regard, several challenges remain for the manufacture of ChG optical elements relative to conventional glass elements. The two major differences between the production of the two types of glasses arise from the fact that: (a) ChG must be processed in an oxygen-free atmosphere, often starting with elemental powders that have been purified for the removal of oxides by thermal treatment of the reagents, and addition of $AlCl_3$ impurity-getters in the melt followed by distillation.²⁸ To maintain IR transparency the glass may not have more than a few ppm oxygen. (b) The vapor pressure of constituents is usually very different, which promotes inhomogeneity in the glass.

The condition (a) dictates batch melting in evacuated silica crucible. Due to vacuum conditions at high temperature, the maximum diameter of cast glass is ~20 cm. For IR applications the tolerance for homogeneity is less stringent than for optical glasses for use in the visible range. Nonetheless, the ChG melt must be rotated or stirred for desired homogeneity. Since common ChG compositions for use at long wavelengths are opaque to the eye, assessment of homogeneity can be problematic. Both of these requirements add to the cost of ChG products, which are made of inherently expensive elements such as Ge.

Recently, the group at University of Rennes has demonstrated success of making $80GeSe_2-20Ga_2Se_3$ ChG by mechanosynthesis, which overcomes the heterogeneity problem. It can be readily adapted for fabricating glass-ceramic of controlled microstructure. In this process elemental powders are ball milled for extended time in an inert atmosphere until they have reacted chemically to a stable state. The reacted powder can be formed into glass by melting and casting, hot pressing or spark plasma sintering (SPS). The whole process takes much less time and lower temperatures, thus permitting the preparation of glass which would crystallize by the conventional melt-quench method. Since the milling is conducted at room temperature, it is plausible that the process can be performed in air, and the brief melting of reacted powder can be done in nitrogen atmosphere.

In general, ChGs are weaker than oxide glasses and their polishing is more difficult. Together with the necessity of isolating the melt from oxygen, the forming/shaping of ChG is more complex. At present the specifications of ChG optical elements are less stringent than for oxide glass elements, but this may change as the

range of products based on ChG expands. So far molding has been shown to be a commercially viable fabrication method for making optical smooth lenses etc., but it must be conducted in a controlled atmosphere.

Several challenges remain for the commercial scale development of ChG,

especially for IR optics:

- SPS appears to be a promising fabrication method for making homogeneous ChG elements. However, the viability of SPS for large scale production remains to be established. A thorough evaluation of this recently developed process and products is needed.
- ChGs exhibit significantly higher dispersion. To compensate for this undesirable effect, complex structures must be fabricated.
- New compositions must be identified which have lower dn/dT .
- A continuous fabrication process needs to be developed for reducing the cost.
- So far defense enterprise has

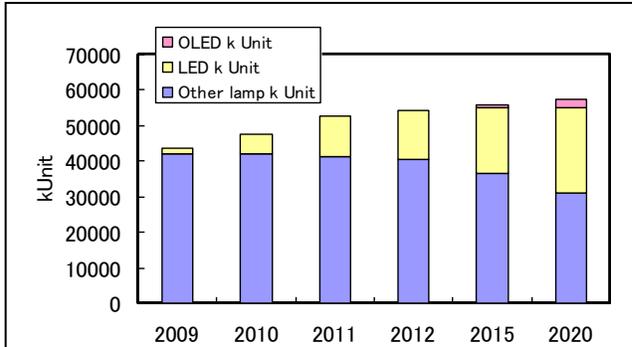


Figure 14.: Anticipated growth and distribution of OLED, LED and all other lighting devices, in the unit of 1000s. (Adapted from the presentation, 'High Refractive Index Glass for OLED Lighting', by T. Murata, Nippon Electric Glass (NEG). For details, see links at http://www.lehigh.edu/imi/TLL_FunctionalGlasses2013.html)

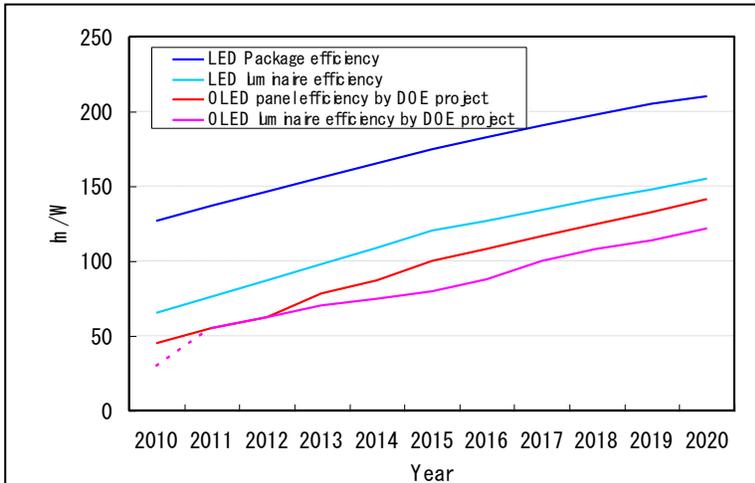


Figure 15. Comparison of LED and OLED lighting devices indicated as efficiency, lumen/W, over this decade. (Adapted from the presentation, 'High Refractive Index Glass for OLED Lighting', by T. Murata, Nippon Electric Glass (NEG). For details, see links at http://www.lehigh.edu/imi/TLL_FunctionalGlasses2013.html)

been the major driver of infrared optic devices. To widely spread this new class of functional glass in commodity market, public relations activities may be needed to clarify incorrect toxicity concerns and develop appreciation for the amazing properties of chalcogenide glasses.

The talk on “**High refractive index glass for OLED lighting**” was presented by Takashi Murata (Nippon Electric Glass (NEG), Japan). In the world, lighting consumes 19% of total electrical energy.²⁹ With rapid industrialization of the developing countries, it is anticipated that by 2020 we

will need about 5,000 TWh of electricity to keep the world illuminated. Incandescent, fluorescent, gas discharge and high intensity discharge (HID) are the most common forms of lighting technologies in use today, with light emitting diode (LED) lighting poised to expand at the fastest rate in the present decade (see Fig. 14). Its key strengths are: long lifetime, high efficacy (lumen/W), high light output, and mature, low-cost manufacturing. Notwithstanding, organic light emitting diode (OLED) technology is coming up with advantages with regard to diffuse lighting, low color temperature and high lumens, especially for large area fixtures. There are clear indications of market penetration by LED lights, but its limitations are recognized when considering the total cost (including diffusors, packaging, safety management, etc.) per luminaire (see Fig. 15). The OLED lights, which are significantly more expensive to manufacture, have much simpler packaging requirements, so that they begin to appear competitive to LEDs when comparing cost/lm – see Fig.15.

A photon generated within OLED encounters two optical interfaces before exiting the device: an internal interface between the conducting indium tin oxide layer (ITO, $n = 1.8$) and cover glass ($n = 1.5$ for currently used off-the-shelf composition), and an external interface between the cover glass and air. The internal reflection at these interfaces limits the available light only to 20% what is produced within the device. Thus there is potential for major improvement in lumens/watt if a greater fraction of light can be harnessed out of the OLED structure. Several strategies have been attempted to this effect by structuring the surface of cover glass such as sand blasting, formation of lens arrays, etc., which would scatter light externally. So far such methods have not been economically viable for the limited gain in efficiency that they produce. A simpler approach from the processing viewpoint is to use the cover glass with refractive index approaching 1.8. Of course, such a glass should be thin to keep the weight down, be manufacturable in large size at low cost, and be scratch-free for high strength. The overflow down draw process of manufacturing large, thin, smooth glass sheets appears to be the choice of making sheets for use as cover glass of OLEDs.

Recently, Nippon Electric Glass (NEG) has developed a new alkali-free glass of $n = 1.64$, which can be formed in 3 m wide, 70 μm thin glass rolls. The use of this as cover glass shows an improvement in efficiency by 10%, which is equivalent to increasing the life time of OLED lighting panels from 5.5 to 6.5 years. These are encouraging results, but at present the cost of such a glass is not known, and there is room for improvement by further increasing the refractive index of cover glass. In summary, OLEDs are expected to become a significant fraction of lighting options, especially for large area lighting. The success of their penetration into market will rely on overcoming several challenges listed below:

- (i) Development of cover glass with refractive index approaching 1.8, which can be manufactured by the overflow down draw method in thin, large size glass sheets.
- (ii) The efficiency for light extraction from OLEDs can be improved also by surface (nano)structuring that is cost effective and does not deteriorate other properties of the cover glass.
- (iii) The cutting of glass sheet must be managed to keep the edges smooth, which determines the flexibility of the structure.
- (iv) There are additional issues that are not related to glass, but they will be important for the consumer acceptance of OLED lights. These include: shorter lifetime related to

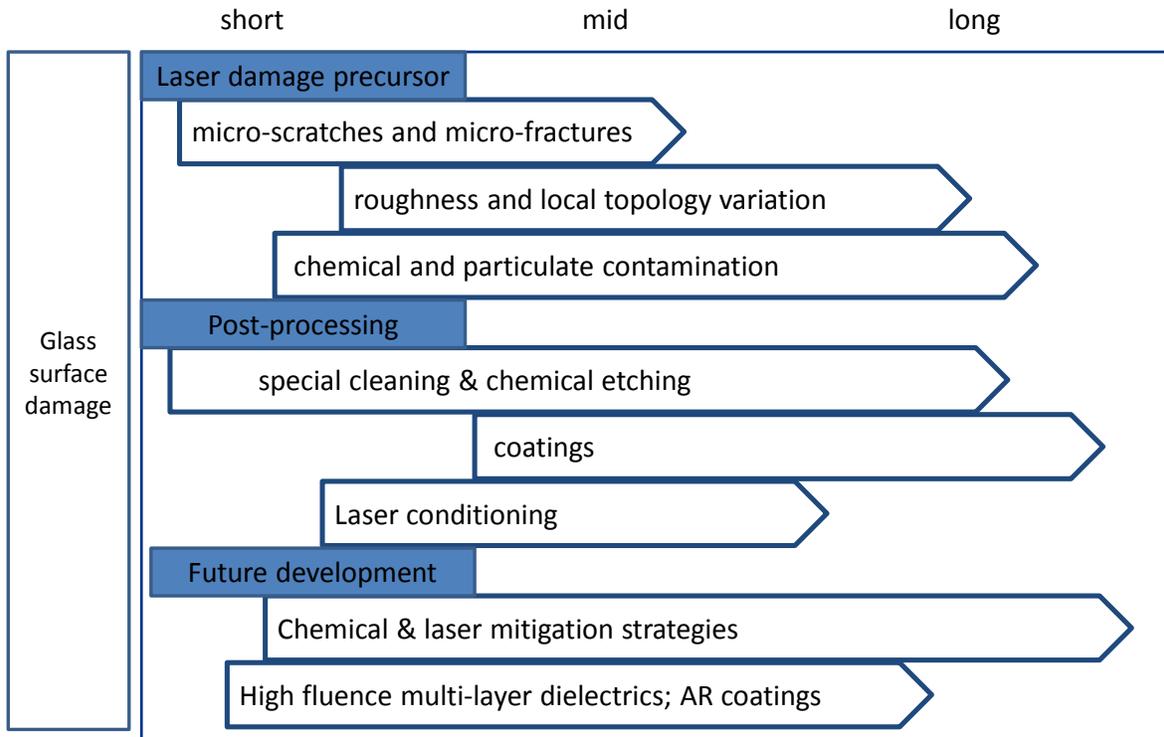
LEDs; significant drooping (i.e. drop in light output with time); and improvement of intrinsic efficiency.

4.1 Summary: Glass Processing in Production

The traditionally used real glass production is fairly complex and consists of many process steps on the way to the final glass product. The well-known simplified version of the process chain may be divided as: the selection of the appropriate raw material for the batch, the melting and forming processes, and sometimes post-processing like coating. In the future, special process topics and added value processes at the end of the process chain will gain in importance while in the classical field of glass production the energy saving and energy efficiency will be in the focus.

Surfaces will play a dominant role in future for more advanced glass products. In extreme, when they are used in laser applications especially at high intensities. There the precursors at the glass surfaces for the laser damage are manifold such as micro-scratches and micro-fractures, irregular roughness, local topology variation, and chemical/particulate contamination. To avoid the damage of the glass surface during use, post-processing operations have to be developed and applied, which can be, for example, special cleaning, chemical etching with HF acid, or more costly processes like the application of coatings and laser conditioning. In the future, such processes have to be investigated in larger detail, and future R&D activities should concentrate more on new chemical and laser mitigations strategies. In particular for higher photon fluences, multi-layer dielectric coatings and stable AR coatings may have to be developed along with new materials for filters. See Roadmap 10.

Roadmap 10. Glass Processing and Production

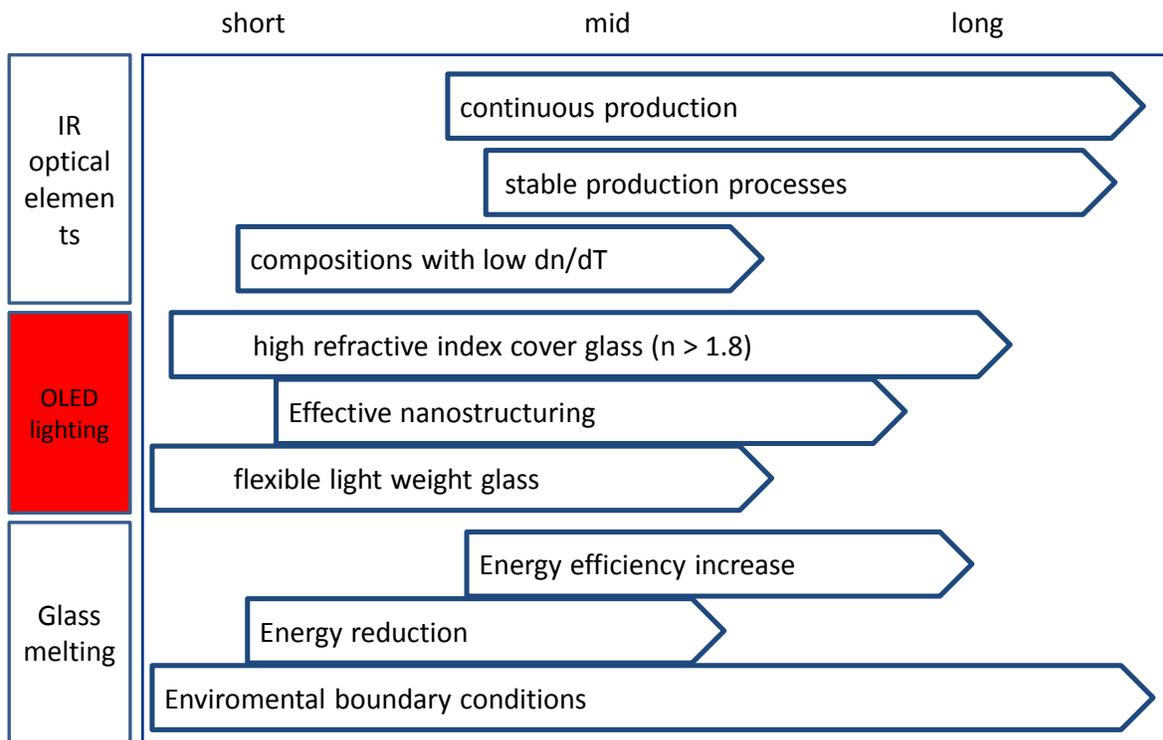


The commercialization of IR optical elements on the basis of chalcogenide glasses has a major challenge. The traditional glass production processes, in particular the melting, cannot be applied directly and new technologies have to be developed. Many potential applications for IR optical elements are at the horizon for example, automobile driver vision enhancement, maintenance and surveillance of operations, industrial process control, firefighting, thermal imaging, weapon guidance and more. But the cost targets can only be realized with a mass production. Therefore, production technologies have to be developed, which work continuously with stable production to a high yield. In addition, material compositions with a lower dn/dT have to be developed and product launch activities have to be initiated for the entrance and penetration into the commodity market. See Roadmap 11.

The traditional glass production technologies have the potential to contribute to improvements of more advanced products in the future. Glasses with special properties can help produce highly efficient OLED lighting systems. The light output of such future lighting system can be improved by the use of high refractive index (>1.8) cover glass (instead of standard flat glass with $n=1.5$), which is possible to manufacture with the classical technology. Flexible, lightweight glasses are of high interest for this new lighting technology as glass is also a candidate as encapsulation material for the optical active system. Here it would prevent the contact between the organics and oxygen or the humidity of the atmosphere. A cost effective nano-structuring of the glass surfaces is another option for improving the efficiency for light extraction from OLEDs, which should be studied in detail. See Roadmap 11.

In the field of classical melting technology advanced processes are possible, in fact needed for advanced glasses or specialty glasses. Many incremental changes and improvements are realized in the production lines in glass industry but also radical new concepts are being discussed publicly. Changes in the society have raised environmental issues in all aspects of technology during the last decade. The future developments in glass melting technologies would need to realize an increase in energy efficiency of the processes, and reduction of the amount of energy consumed, finally leading to a cost reduction of the melting processes. See Roadmap 11.

Roadmap 11. Glass Processing and Production



5 Influence of the surface on glass properties

In the field of energy technology and information technology glass surface plays a crucial role for many applications. Its fundamental understanding is needed for controlling the processing of glass as well as improving the performance in practice. This chapter examines the role of surface in establishing the mechanical properties of glass under various conditions.

Satoshi Yoshida (University of Shiga Prefecture, Japan) introduced **“Fundamentals of indentation cracking in glass: A measure of strength?”**. Brittleness is one of the most crucial concerns with a glass product. The glass sheet for LCD substrate is becoming thinner and thinner year by year, and the cover glass sheet with enhanced mechanical resistance is now required for tablets and other mobile devices.

Therefore, a simple method of evaluating the mechanical performance of glass is urgently needed for users and suppliers of such glass products. The indentation test is one of the attractive tests, which is simple and easy to perform. However, a relation between indentation cracking and macroscopic fracture of glass still remains poorly understood. This is due to a lack of understanding of the mechanism of crack initiation and/or propagation during the loading and unloading parts of indentation cycle. In addition, the variation of crack morphology with composition makes a comparison of crack-resistance or strength of different glasses difficult. In order to resolve this fundamental problem, it is essential to evaluate compositional variation of indentation cracking and to clarify the mechanism of elastic and/or inelastic deformation of glass prior to its fracture.

Sharp diamond indenter creates a permanent impression on glass such as an indentation imprint or a scratch groove. The mechanism of irreversible deformation of glass can be divided into mainly two modes: shear flow and densification. The focus of the talk was on the degree of densification, which plays an important role on the residual stress around the indentation imprint. The ratio of densified volume to total indentation volume increases with decreasing Poisson's ratio of glass. Accordingly, the residual stress after unload depends on glass composition. Not only the residual stress but also the stress distribution around the indentation imprint is important for understanding the driving forces of indentation cracking. One quantitative approach uses micro-photoelastic or micro-birefringence property of glass. The effectiveness of this technique was shown along with some results of stress mappings around the imprint both during and after indentation. The elastic stresses during loading were in good agreement with the analytical solutions, and the analysis showed a less compositional variation. On the other hand, the residual stresses after unloading showed a remarkable composition dependence. Although this technique is still under development, it should become valuable for quantitative discussion on indentation cracking in glass.

The central issue is to understand the **contact damaging** mechanisms at the atomic level of silicate glasses, and how it may depend on:

- The glass chemical composition and molecular structure
- The nature and geometry of the damaging body
- The environment (temperature, relative humidity (RH), etc.)
- Other parameters (thermal / chemical tempering, residual indentation stresses, loading rate, etc.)

This fundamental information would open the door to the formulation of more contact damage resistant glasses. Since the existing pristine glasses are strong enough, the development of stronger glass should not be the focus; it is more important to develop glasses that retain higher strength after surface contact. It would be especially critical for the development of touch sensor technologies. This challenge will require the development of new experimental techniques for characterizing the mechanical state of a sample, as well as its atomistic modelling. University researchers are expected to play a major part in these developments, especially in the latter.

Other questions regarding the strength of silicate glass include: cost effective strengthening process for thin and ultrathin glass, low temperature edge strengthening (edge damage resistance enhancement) process, integration of new

cutting/drilling/grinding/polishing/finishing processes, mechanisms of strength degradation or strengthening specific to glass fibers. In a way, these issues are secondary from a scientific point of view because they would theoretically benefit from any advance in the above mentioned needs. Nonetheless, they are blocking the current technological development of new applications and new glasses, and therefore should be addressed in parallel. A strong driver for glass strength improvement is reduction of weight, which in turn is driven by cost and scarcity of resources such as energy, uncommon elements, and impurity control.

Seong Kim (Pennsylvania State University, USA) addressed “**Surface chemistry of glass – interfacial water and mechanochemical properties**”. The behavior of adsorbed water on a multicomponent silicate glass is very different from that on a pure silica surface. The structure and reaction of water films on silicate glasses can drastically vary depending on the surface composition as well as the process through which the surface is created. The degrees of freedom for creation of hydrogen bonding networks with both molecular water and adjacent silanols on the surface is very sensitive to the silanol group distribution on the surface. Moreover, the presence of metal ions and other electrolytes in multicomponent silicate glasses can modify the water network, and can also create or annihilate local stress within the silicate network. Thus, the surface reactivity and durability of glass can be linked to its composition and Si-O-Si network structure through the interfacial water property.

The interfacial water structure on soda lime silicate glass was studied in humid ambience at room temperature using sum-frequency-generation (SFG) vibration spectroscopy which can probe the interfacial water layer without spectral interferences from the gas phase water. The soda lime glass surface exposed to water vapor shows three sharp SFG peaks at 3200cm^{-1} , 3430cm^{-1} and 3670cm^{-1} in SFG, which is drastically different from the SFG spectra of the water layers on fused quartz glass and the liquid water/air interface. The sharp peak at 3200cm^{-1} is believed to be associated with the hydronium ions in the Na^+ -leached silicate glass surface. The 3200cm^{-1} peak intensity varies with the relative humidity, indicating its equilibrium with the gas phase water. Since it is in equilibrium with the gas-phase water activity, the hydronium ions would not be readily detected in vacuum conditions. If the hydronium ions are occupied in the Na^+ -leached sites, then they could produce compressive stress in the silicate glass surface. An increased wear resistance of soda lime glass surfaces was observed in near-saturation humidity conditions. These observations support the importance of interfacial water structure on mechanochemical behavior of glass surfaces.

For most glass applications these fundamental observations are highly relevant, since water is always present in the atmosphere. In particular, the effect of the surface state on the friction and scratch-resistance is of high interest. For example, the surface state of glass after rubbing can be changed by the humidity, even when changes are observed in low load. These situations (low applied load with certain humidity) exist everywhere for glass products and may modify/damage the surface, which can be the origin of the ultimate breakage. So it is of high interest to understand the initiation of the defect on the glass. A key challenge of such studies is that the existing ambience of glass products is uncontrollable and the nature of the chemical reactions can be changed by the respective ambience. Thus if an interesting result is

found at certain ambient, it could be difficult to apply the same directly different glass products.

In summary, the water activity at glass surface is in equilibrium with the gas phase water, which can be quite different from that at SiO_2 surface. At high relative humidity, H_3O^+ ions seem to form in the interfacial region. Scratch resistance under shear is a mechanochemical effect (not just mechanical) and is different from stress corrosion or crack propagation. It is a function of both the vapor and counter-surface chemistry.

The discussion on proton conductors was initiated by Steve Garofalini, Rutgers University, USA with a presentation on “**Proton behavior at glass/water interfaces: implications on reactions and proton transport**”. Electrochemical studies have shown enhanced proton transport in nanoporous amorphous silica containing water in comparison to proton transport in bulk water. While generally attributed to hydronium ions, such studies provide no specific data regarding the mechanisms causing the differences between the nanoconfined water and bulk water and, most importantly, do not address the role of the water-silica interface on such behavior. Because of the structural heterogeneity of the amorphous silica surface, large-scale simulations are required to include the effects of this heterogeneity on proton adsorption and protonated-site lifetimes. Achieving an accurate description of proton transport in such atomistically large and structurally complex interfacial systems precludes the use of ab-initio calculations, which are limited by both size and time constraints. To address the behavior occurring at the water/silica interface, a dissociative water potential was developed and used, which matches many properties of bulk water and the high thermal expansion of nanoconfined water. It shows proton transport involving Eigen and Zundel complexes consistent with ab-initio calculations, and hydronium lifetimes in bulk water consistent with experiment. It also shows the appropriate dissociative chemisorption of the water molecules on the silica surface and the enhanced formation of hydronium ions at these surfaces, similar to ab-initio molecular dynamics simulations of small systems. In addition to the formation of surface silanol (SiOH) sites via dissociative chemisorption of the water molecules, where protons are strongly bound, the simulations show the location of weakly binding highly acidic proton adsorption sites on the silica surface that contribute to enhanced proton transport beyond that observed in the water phase alone. The simulations provide a detailed molecular understanding of enhanced proton transport in nanoconfined water seen experimentally.

For molecular dynamic simulation studies the proton transport behavior at glass/water interfaces can be split into several parts:

- the development of a dissociable potential model for water,
- the structure at the water/silica glass interface,
- the transport of water at the interface,
- the collision cascade induced defect formation and associated relaxation and effect of water in silica glass.

For the potential development an extensive comparison with experimental and ab initio data of water is necessary due to the complex nature and difficulties in modeling water and the water/silica system. The existence of water in the form of hydroxyl group, hydronium ions, and water molecular species and their transient lifetime at the

glass/silica glass interface plays a crucial role and proton transport at the interface has to be investigated in detail. Additional topics of interest include: radiation induced behavior and the effect of water on radiation induced damage remediation, the duration over which each forms of water exists.

The main challenges for future development of new simulation methodologies and how to combine simulation and experimental studies include:

1. **Extension of potential models to include multi-component glasses.** These glasses include alkali silicate glasses, aluminosilicate and borosilicate glasses that are common to practical glass compositions. Water interactions with these glass compositions have much practical significances..
2. **Effect of water on mechanical behavior such as crack formation and propagation.** Water plays a significant role in these phenomena.
3. **Effect of water on radiation damage.** The observation that water inclusion leads to increased damage in radiation environment raises the question whether glass is a suitable material for waste packing. The observations from simulations would need further supporting evidence..

5.1 Summary: Glass surface and properties

In most of the final products of energy technology and information technology, the brittleness of glass is one of the most crucial issues. The glass is becoming thinner every year, and many products require improved mechanical performance. Therefore, various phenomena at the surface are becoming increasingly more important, and a fundamental understanding of surface processes is essential. The basics of strength and cracking process, the mechanochemistry of the surface which depends on the water vapor conditions, and the effect of water on different surface damages need to be studied in greater detail.

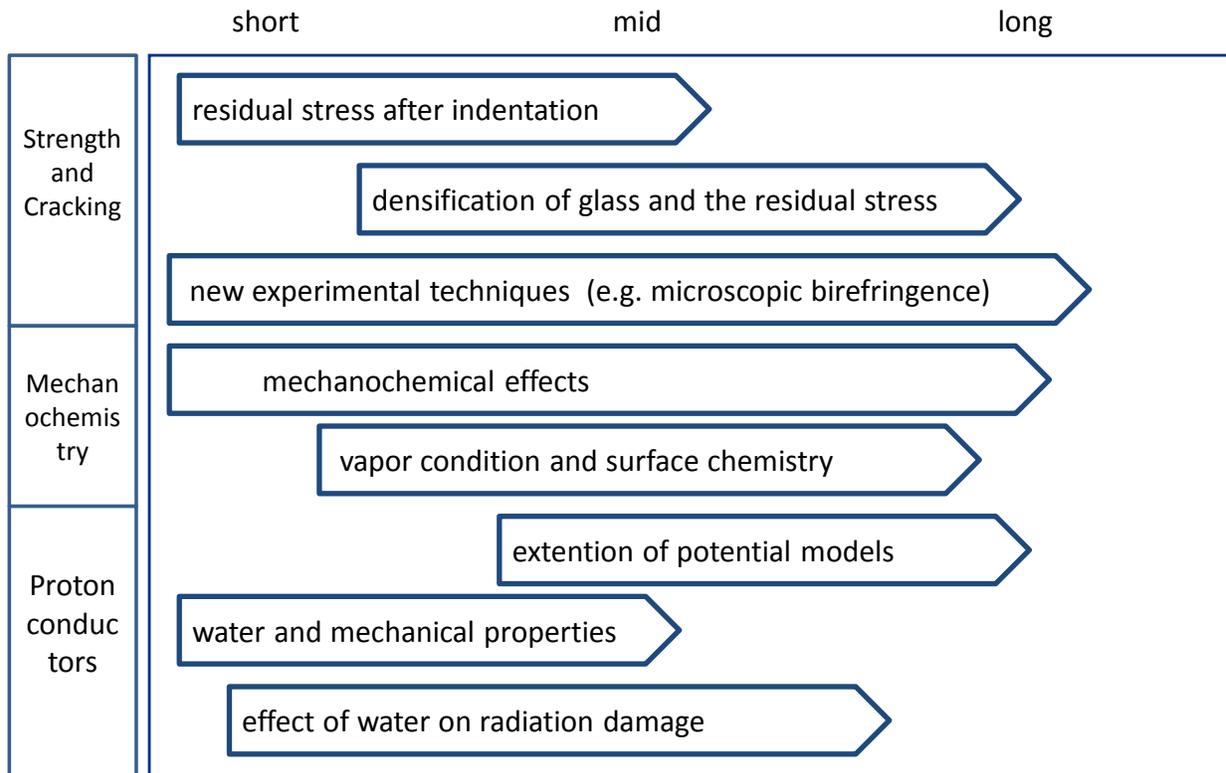
Many scientific questions remain to be answered to obtain a better understanding of the mechanical behavior of glass surfaces. For example, to describe the contact damage at atomistic level, following parameters need to be considered: the glass chemical composition and molecular structure, the nature and geometry of the damaging body, the environment conditions (T, RH), etc.. Future scientific investigations should focus also on the residual stress after indentation, the correlation between the densification of glass and the residual stress, and new experimental techniques for quantifying local stresses. See Roadmap 12.

A key challenge of future research in this field is a better understanding of the mechanochemistry of glass surfaces. In general, glass products are exposed to a range of humidity and temperature, which affect the mechanochemical state of its surface. Therefore, a thorough understanding of correlation between surface mechanochemistry and the scratch resistance is needed for different glass types, besides the stress corrosion or crack propagation as a function of environmental conditions. See Roadmap 12.

Furthermore, we need new simulation methodologies that produce experimentally verifiable results. The combination of simulation and experimental studies will help understand the nature of complex water/glass interactions. This goal will require an extension of potential models which incorporate key glass elements and a

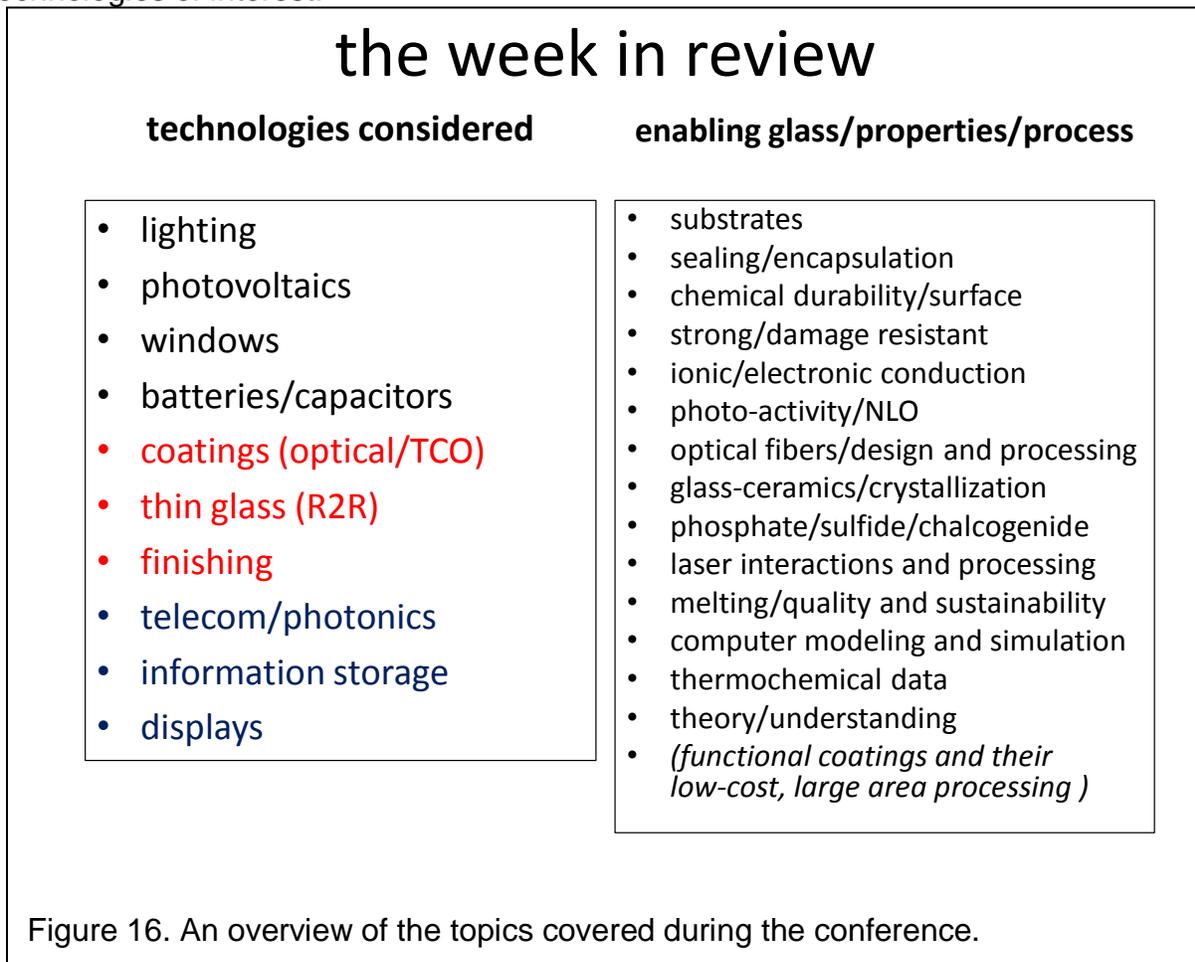
realistic description of the effect of water on mechanical properties, radiation damages, etc..

Roadmap 12. Glass Surface and Properties



6 Summary

The final session of conference consisted of a panel discussion led by industry leaders from Corning, NEG, PPG, SCHOTT and St. Gobain. Carlo Pantano opened the discussion by listing the technologies and enabling glass properties and processes considered during the week. Then the panelists presented their assessment of the most pressing R&D needs for achieving the full potential of glass for the advancement of energy and information technologies. Together with them the audience debated and discussed the priorities and approaches for accomplishing the goal of the conference, which was to identify the most important applications for glass in energy and information technologies, and the scientific issues and engineering hurdles that are limiting its advancement. Below in Fig. 16 is given a summary of various R&D needs and opportunities pertaining to the most promising applications of glass in the two technologies of interest.



The needs and opportunities for glass in solid-state lighting, photovoltaics, energy-efficient windows and batteries were evaluated in case of energy technology. For solid state lighting, key challenges are development of: (a) glasses for higher refractive index substrates and encapsulation of (organic) light emitting diode devices (LED and OLED), and (b) large area coatings for glass with transparent oxide coatings

(TCO), OLED materials, and metal films. The barrier properties of glass against water and oxygen ingress are especially important for OLED whereas the high index glass would enhance light extraction. The concept of an *integrated glass substrate*, already coated with the anode and light extraction layers, is one possible approach for flat glass producers to lower costs for this fast growing market.

For photovoltaic (PV) applications, the glass market has potential to grow further, if cost can be reduced. It is used primarily as a cover glass for crystalline Si PV, and as both substrate and superstrate in the case of thin-film PV. In general, improvements in optical transmission, stiffness and strength can help, especially if combined with thinner, lighter weight glass. However, lower cost coating and secondary processing of float glass may be more important here. It is noteworthy that more efficient PV thin film materials are emerging. They can change the requirements for the glass, but the price to performance ratio is not yet favorable for existing materials such as CuInGaS and CdTe. In the case of other solar energy conversions technologies, such as concentrated solar power (CSP) and glass bioreactors, transparent coatings on the glass are critical for light and heat management, protection from fouling, light transmission and service life. The optical transmission of the glass is important for PV, CSP and bioreactors, which can be improved by lowering the Fe impurity content of the raw materials, by using thinner glass, or some other innovative approach.

For energy efficient buildings, coated glass already plays an important role in low-E windows, but for smart windows, glasses coated with *active* materials are needed, which can respond to the light intensity (photochromic), temperature (thermochromic), electric field (electrochromic) or redox gas (gasochemical). These coatings include metal films, heavily doped wide band gap semiconductors, and *nano-carbons* such as carbon nanotubes, graphene monolayers, and C60 buckyballs which can form transparent conducting films in the near-IR. They also include semiconducting phase change materials such as VO₂ that can switch from an IR-transparent semiconductor to an IR-reflecting metallic phase at T>68C.

In the aforementioned energy technologies, and as well in displays and integrated optics, coating of the glass with optical or electronic thin film coatings is common. Perhaps most pervasive is the deposition of transparent conducting oxide thin films such as Sn-doped indium oxide, F-doped tin oxide or Al-doped zinc oxide for thin-film PV, electrochromics, displays and touch screens. In most cases, the surface chemistry of the glass is often passivated with a barrier layer to minimize interactions with the dopants. The coating process and physical characteristics of the glass surface must be uniform over large areas. For large and small electronic displays, patterning of the films is also required. In this context, the recent development of thin, flexible glass is significant. Since displays and electronics are becoming lighter, thinner, and more flexible, the choice of substrate can be critical to their overall optimization. The substrate directly affects possible improvements in the design, material selection, fabrication processes, weight and performance. Currently, there are several producers of such thin glass with thicknesses of the order 30-200 μm. At the lower end of this thickness range, roll-to-roll processing of thin film deposition and device patterning is possible with potential benefits not only for displays but also for energy efficient windows, lighting and photovoltaics. The capability for continuous vacuum deposition, photolithography, laser patterning, screen printing, slot die coating, and lamination has already been

demonstrated. Another benefit of flexible glass is its mechanical reliability. The edge strength/resistance-to-tearing is maintained by an edge finish, but otherwise the mechanical behavior of this glass is unique and favorable. In most loading conditions, it will bend rather than fracture.

For energy storage, solid state batteries are the primary target although capacitors can also have a significant impact especially with the advent of low-alkali boroaluminosilicate glasses. Glass and glass-ceramic ion conductive materials could provide safer and higher energy density electrolytes for the proposed *all-solid-state Li ion battery* which is expected to yield more than an order of magnitude increase in the energy and power density of lithium cells. Such solid state lithium batteries eliminate capacity lowering carbonaceous cathodes, flammable liquid electrolytes that foster dangerous metallic lithium dendrites, and low capacity high mass transition metal oxide cathodes. The core scientific and technological breakthroughs enabling such all-solid-state batteries will be the development of new solid electrolytes that are low cost, green, stable, and exhibit high ion conductivity. The wide compositional ranges of glasses, their relatively low cost and ease of fabrication, and their chemical and electrochemical durability make them a very promising candidate. But safety remains an issue with Li, especially metallic Li anodes, and for this reason there is increasing attention being paid to all-solid-state Na ion batteries. Some new materials and processes were described for such Na-ion battery systems. A non-oxide “sulfide glass system”, made by melt quenching or mechanical milling of $\text{Na}_2\text{S}+\text{P}_2\text{S}_5$ glasses, is of interest for the electrolyte in room temperature Na batteries, while chalcogenide glasses are being considered for anodes. A new low-cost cathode material, $\text{Na}_2\text{FeP}_2\text{O}_7$, fabricated by a glass-ceramics process is also being developed for this Na-ion system. At the same time, LiFePO_4 glass ceramic cathodes are pursued for Li-ion batteries.

Fundamental to the use of glass and glass-ceramics for battery electrolytes and cathodes, as well as for high energy density storage capacitors, are their dielectric and ion transport properties. For an effective improvement in ion conducting glasses, the role of short and intermediate range order structure in ion transport needs to be better understood to optimize the design of new super-ionic glass conductors. Fast lithium ion conducting glass-ceramics are also promising materials for all-solid-state lithium batteries, although the high resistivity of the grain boundaries in glass-ceramics is an issue to be resolved. Similarly, the milled and cold-pressed sulfide and phosphate battery materials are plagued by limited understanding of ion transport across particle boundaries. For high energy density storage capacitors, ion transport plays an opposite role and must be limited to prevent dielectric breakdown. The new very thin flexible glasses offer such high dielectric breakdown strength, but the composition is not yet optimum for maximum energy density.

Hermetic seals are required in many energy systems including electrochemical devices for energy conversion and storage, energy efficient vacuum and gas filled windows, and for high temperature systems. Oxide glasses are often the materials of choice for these applications because they offer a wide range of engineering properties (thermal expansion, viscoelasticity, etc.) that can be tailored, and can be processed in many ways (screen-printing, tape-casting, sintered preforms, etc.). Similarly, improved mechanical strength and damage resistance are required for many applications including glass seals, glass substrates and coated glasses. The recent

commercialization of ion-exchanged glasses is already enhancing an increased use of glass in these technologies. Nevertheless, sharp, high-rate contact damage remains a challenge that will require better understanding of localized plastic deformation, friction and the mechanochemical effects, in general.

In the sessions concerning information technologies, the presentations addressed optical fibers for communication and lasers as well as the use of femtosecond lasers for fabrication of integrated optics and memory devices for photonics. The tremendous growth of the internet has created the need for higher bandwidth components. To operate at bit rates beyond 150 Gb/s, optical communication systems will have to process signals entirely in the optical domain. All-optical signal processing means the control of light by light, which is possible only in a nonlinear optical materials. To minimize propagation losses, there has been a progressive utilization of longer wavelengths (from 0.85 μm to 1.3 μm to 1.5 μm). Thus, the challenges for developing the next generation of telecommunication systems are not only a better understanding of nonlinear optical processes, but also a parallel development of new optical materials and optical fiber designs that operate in the near-IR. Microstructured and nanoscale optical fibers offer the opportunity to guide and manipulate light in new ways with the goal of creating novel fiber-based optical devices. The first photonic crystal fiber (PCF) with a solid glass core emerged from the drawing tower in 1995, and fiber optics entered a new phase because more than 99% of the guided mode field resides in the hollow regions of the fiber, and thereby the effective transmission loss can be many times lower than that of the glass itself. Ultra wideband transmission and multispectral amplification, as well as space division multiplexing with multicore fibers, are emerging applications for these fibers. But they are also being exploited for *lab-in-a-fiber* by using the PCF as a microfluidic channel that guides light to optically manipulate particles and cells.

Optical microfibers and nanofibers are glass fibers with diameters close to or smaller than the wavelength of the guided light. These new fibers, usually fabricated by redraw of larger fibers, open the door to devices based on near-field optics, plasmonics, and optomechanics; they also enhance nonlinear optical effects for photonic engineering. Likewise, nanofibers are being developed as optical sensors, but require engineering and fabrication of the nanoscale "optical-chemical interface".

The possibility to fabricate integrated optics devices using femtosecond lasers, and the associated photosensitive properties of glasses, is a very active field of research which can accelerate the development of all-optical photonic communication and data storage systems. For this reason, the study of photosensitivity and laser induced modification and damage in glasses has attracted considerable interest, enabled by advent of high power pulsed lasers. The nonlinear nature of the absorption confines any induced changes to the focal volume making it possible to both transform properties and/or micromachine geometrically complex structures in three dimensions. Several demonstrations of waveguide and (nano)grating fabrication have been made but better understanding of the fundamental laser-material interactions is still needed, especially concerning the competition between thermal and electronic effects of high intensity laser irradiation. In this regard, many different glasses and transparent glass-ceramics including phosphates, chalcogenides, and tellurites are being studied both to understand the laser-material interactions and to find optimal materials for device

performance. Based on work to date, a combination of different glasses will be required to meet all the requirements of such systems. Fortunately, it seems that these less-common glasses are compatible with silica based telecommunication fiber, and could provide for low cost fabrication by laser processing.

The non-linear optical (NLO) properties of these less-common glasses play a role in both the femtosecond laser treatment and fabrication of devices, as well as in their performance in all-optical photonic systems. Here, too, complete understanding is lacking, but the field is very active in the study of fast intensity-driven index changes, second and third harmonic generation, stimulated Raman emission and the multiphoton absorption. This fundamental research has also encouraged the study of less common glasses such as tellurites, transparent glass-ceramics, metal and semiconductor nanoparticle glasses and glass/polymer hybrids. The transparency of these materials and the magnitude of the NLO effect are still limited, but several specific glass and glass-ceramic compositions are now approaching practical applications. More research is needed to clarify whether such materials can outperform thermal poling for maximizing second harmonic generation, to understand the role of their short and medium range structure, and to engineer the plasmon resonances in nanoparticle glasses and glass-ceramics. To be sure, fundamental study and collaboration between optical physicists, material scientists, and optical engineers will be required to meet the challenges of *all-optical communication systems*.

The following topics were considered as nascent topics, unsolved problems or open questions, which should be taken up for exploiting the full potential of glass in e applications:

- Continuous production of chalcogenide glass.
- Reevaluation of the “old” renewable energy technologies as energy will remain a challenge in the coming years
- Exploration of epitaxial growth on glass.
- New glass composites.
- Functional glasses made by novel surface treatments
- Surface of glass – it is becoming one of the most important factors for the performance of glass, yet there is very limited R&D activity in this topic,.
- Coatings - which are expected to be dominating the use of glass in the future, yet there does not appear to be any plans for its long term R&D
- How to combine different functionality on glass?
- How to increase and coordinate the limited glass R&D activities?

Besides scientific and technical topics the boundary conditions for glass research were also considered in the panel discussion. The improvement of the cooperation between industry and academia was one aspect, since the participants of the conference were coming from both constituencies. It was agreed that in some countries examples for joined labs for glass research exist (in France with CNRS and in Japan with NFG), but in general joined research activities are rare. Reasons for such lack of interaction are different time scales for R&D, different working styles and sometimes the R&D topics. The most industry activities are short-term R&D actions, often proprietary and have an intense competition in the business. In addition, in this type of R&D, aspects of cost reduction, quality improvement, and efficiency improvement are

included, which are not suitable for research in academia. Nonetheless, even in this short-term R & D, basic research for relaxation, strength, diffusion, crystallization, refining, solubility, viscosity, homogeneous, etc., is very important and can be carried out without compromising confidentiality. On the other hand, some R&D topics appear to be inherently unsuitable for close cooperation. For example, melting is a very important issue in glass making, but it is generally solved by glass companies alone; researchers from other fields are often not interested in that issue.

It was felt that some medium-to-long term R&D industrial research can be conducted more profitably through cooperation with universities. For example, long term research for new functional glasses is needed in many glass companies; often only limited expertise and knowhow for that research field is available in traditional glass companies. To maximize the benefit, such research may be conducted collaboratively. A fraction of these activities can be part of larger project, taking advantage of the public funding available for basic research. Another scenario of industry-university collaboration is via sponsorship of doctoral studies by industry. In this regard, a few PhD thesis titles were mentioned: "Surface corrosion of different types of glasses", "High through-put screening of materials", "Manufacturing of new glasses", "Accurate measurement of temperature in glass melts", etc.

Another broad topic of the panel discussion stressed the image of glass in the society in general and engineering education in particular. Often it seems necessary to explain how useful glass is to the modern society including the world of scientific research. More aggressive public relation actions are needed to change the image of glass as the 'old', 'common' material, rather than an enabler of high-tech solution to today's challenges. Possible ways of rectifying the current public perception can be material alliances, advanced company videos, internet platforms (see e.g. <http://www.friendsofglass.com>) or an IMI discussion forum. In addition, distinctive aspects of glass should be introduced starting in middle and high schools. At present glass research does not appear attractive to most young researchers in academia, as there are few incentives for its pursuit in most countries.

Finally, the feedback on both the content and format of the conference was very positive. The participants strongly recommended organizing follow up meetings along similar lines. For future, they proposed focusing on glass for biomass and biomedical industry, combining with the progress of bioceramics. It was further recognized that for complex applications such as displays, photonics, electronics, environment, energy, etc., scientists with background in the field of glass alone cannot formulate the most optimum research program. It is necessary to grasp the technical details of devices, available tools for its fabrication and for characterizing its performance and have some ability to assess the emerging needs and trends in the society. For this reason it is important to also invite the specialists of related fields, who can help establish the target properties and requirements to be provided by the glass of the future.

Acknowledgment

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Appendix

Pointers for Discussion Leaders (DL)

Keynote Topic Discussion Points

Material questions:

- Why glass for this application?
- What other materials could serve this purpose?
- What trends will influence product development in the future? How will the products change?
- How will product trends impact the future use of glass and property/processability requirements?

Key challenge/Key breakthrough questions:

- What are the **key scientific challenges** related to the topic of your presentation, and more generally the field of your expertise?
- How critical are they to the advancement of the relevant technology?
- Can you identify whether the challenge is with regard to limitations of specific property, performance or fabrication process? Establish target values, where possible.
- What would be a **key breakthrough** and when might it occur?
- How are these breakthroughs likely to occur? University discovery? Industry? University-Industry collaboration?

Success questions:

- What will be a topic stating an **exceptional success** to be published in a well-known high-ranked research journal in 2025 concerning your R&D field?
(please give a title of a publication in 2025, you would like to read)

Related Broad Discussion Points

Future R&D directions questions:

- What are the most **critical scientific questions** (be specific and list not more than 2 or 3 per topic);
- With the given/limited R&D resources, on which R&D topics should we concentrate/reinforce? Which activity should be reduced?
- How much glass research is needed or optimum?
- What kind of education is needed to enable glass research?
- What are strategies for better communication and collaboration in the glass community?

Boundary conditions questions:

- Which changes in boundary conditions are foreseeable in your R&D field (legal, economical, ...)?
- Do you see a possibility to influence/change/improve the boundary conditions (funding, networks,...)?

Glass community questions:

- which actions do you suggest to improve the situation in your field?
- More lobbying activity in the political arena?
- topical position papers?