Infrared-Transparent Conducting Copper Antimony Oxide Films

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Motivation

Transparent conducting oxides (TCO) are a novel class of materials with potential in a variety of applications. In particular, infrared(IR)-transparent materials could be used as electromagnetic-interference shielding for IR-windows and missile domes or as electrodes on the active region of IR-sensors. In either application, understanding the production process and resulting material properties is important as small changes in the growth conditions can dramatically influence the film's performance.

Spinel (AB_2O_4) and delafossite (ABO_2) structured materials have been shown to exhibit favorable transparency and conductivity. In particular, it has been suggested that any combination of a monovalent or divalent A metal (such as Cu, Ag, or Pt), a trivalent B metal (such as Al, Ti, or Cr) and oxygen may produce the desired properties.[1,2] To that end, this investigation is focused on ascertaining if copper antimony oxide, a previously uninvestigated system that meets the valency requirements, also possesses TCO properties.

(Left) **Figure 1.** Seeker missile dome developed for the Joint Air-to-Ground Missile.[3] TCO films can be used to provide electromagnetic-interference protection for the components within the dome.

(Right) **Figure 2.** FT-IR pyroelectric sensor.[4] TCO materials can be used as electrical contacts without compromising the active area of the sensor.

Goals

The overall goals of this investigation are to: first, determine if copper antimony oxide exhibits high IR-transmittance and high conductivity like other TCOs, and second, to explore how the properties change as a function of copper-antimony ratio, oxygen partial pressure, and film thickness.

Approach

Film Synthesis:

A sputtering system equipped with two 2-inch magnetron guns was used to co-sputter from a commercially pure 4 wt% Sb, $Cu_{98}Sb_2$ target and a 99.999% purity Cu target onto rotating IR-transparent, one centimeter square, KCl substrates in an reactive $Ar\text{-}O_2$ mixture with a total pressure of 4.0 mTorr. Chamber base pressure varied between 7 x 10^{-7} Torr and 4 x 10^{-6} Torr.

Due to difficulties of target poisoning due to oxide formation while DC sputtering in a reactive environment, all CuSb depositions were conducted using chopped input power at 20 kHz (90% duty cycle), and all Cu depositions were conducted using an RF power supply.

Film Analysis:

Films were analyzed, at ambient conditions, for IR-transmittance, conductivity, and thickness.

IR-transmittance measurements were made utilizing a Fourier Transform-Infrared (FT-IR) spectrometer focusing on the mid to long-wavelength infrared regime (5 µm to 12 µm) which are typically used for the previously noted applications.

Conductivity measurements were made using the four-point probe method, seen below, in order to eliminate error due to the impedance of the measuring device.

Thickness measurements were made by tearing the bulk of the film with a carbon tape strip to expose a step drop between the film surface and the KCl substrate. The specimens were then coated with 5 nm of iridium, for reflectivity purposes, and the step height was measured using an optical profilometer.

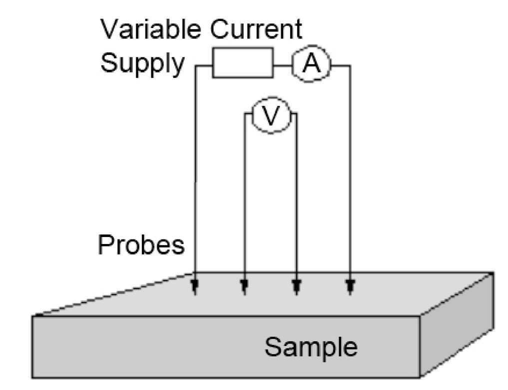

Figure 3. Four-point probe method[5]

Results

Effect of Thickness

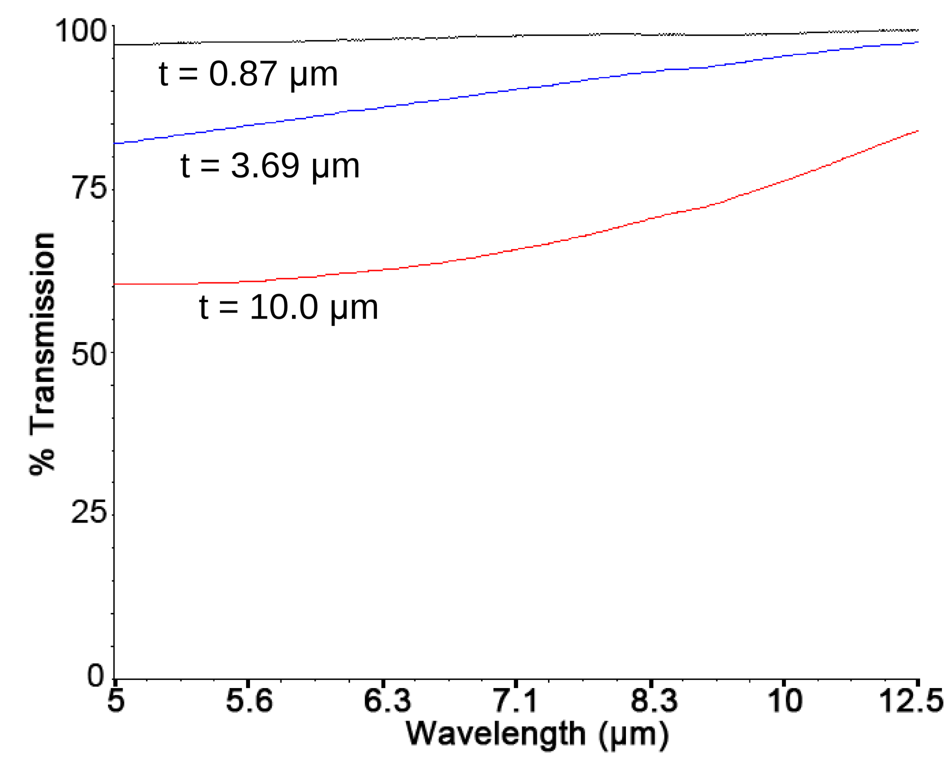

Figure 4. FT-IR spectra for $Cu_{59}Sb_1O_x$ films of 0.87 µm, 3.69 µm, and 10.0 µm.

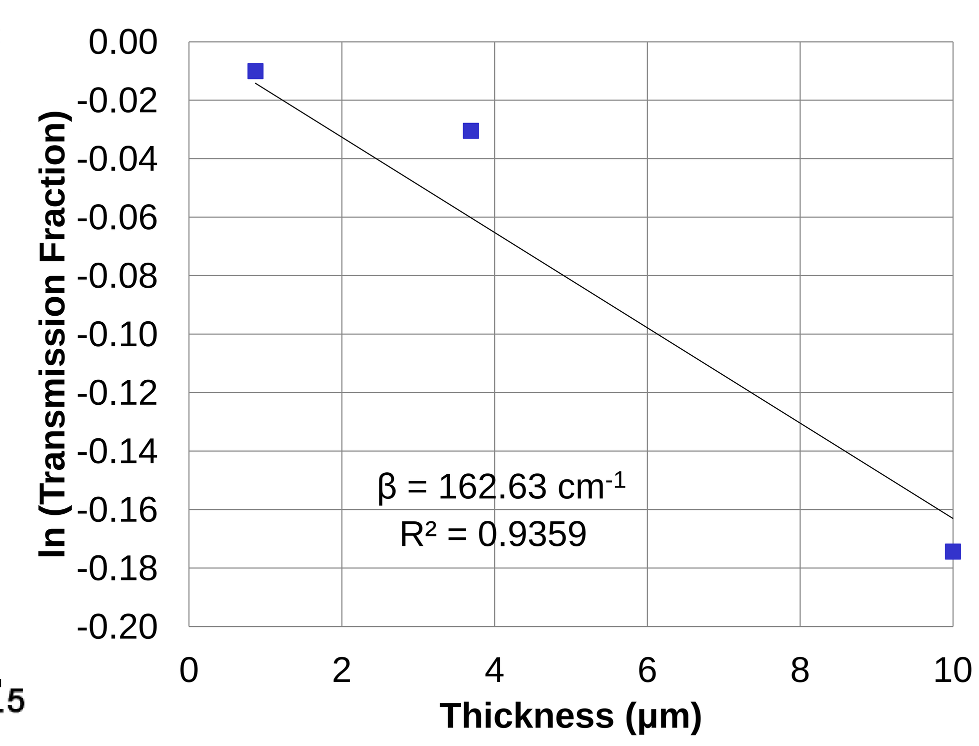

Figure 5. Log plot of transmission fraction versus thickness with the expected relationship shown.

Figure 4 shows an example data set comparing IR-transmittance versus wavelength for three film thicknesses. Notably, as wavelength increases, the films become more transparent. By extracting the values at a single wavelength (12 µm) and plotting versus thickness, Figure 5 can be generated. The theoretical expected result (from $I'_T/I'_0 = e^{-\beta x}$) has also been plotted. Using this analysis, the $Cu_{59}Sb_1O_x$ film was found to have an absorption coefficient, β, of 162.63 cm^{-1}.

Effect of Cu-Sb Ratio and O_2 Partial Pressure

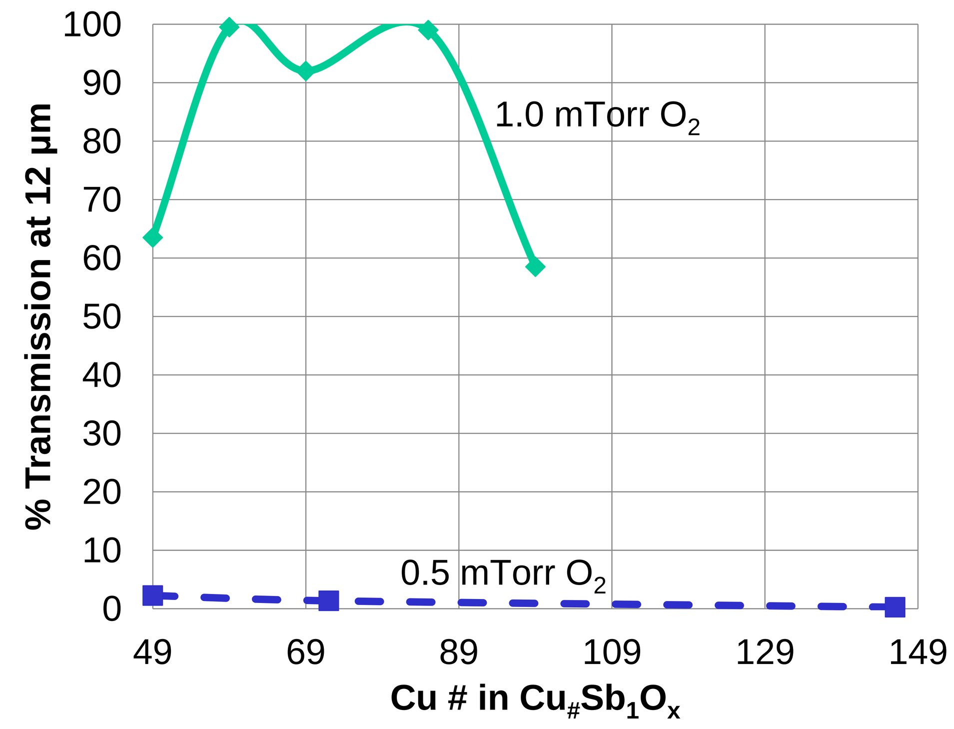

Figure 6. Comparison of % transmission for $Cu_xSb_yO_z$ films with varying Cu-Sb ratios created in 0.5 mTorr O_2 (350 nm average thickness) and 1.0 mTorr O_2 (900 nm average thickness).

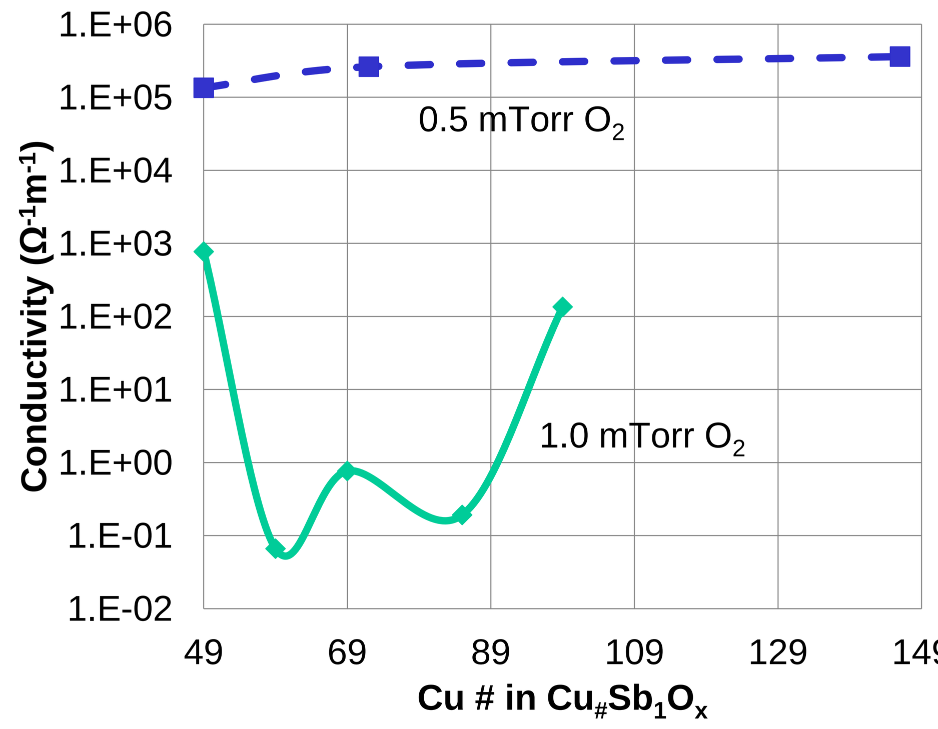

Figure 7. Comparison of conductivity for $Cu_xSb_yO_z$ films with varying Cu-Sb ratios created in 0.5 mTorr O_2 (350 nm average thickness) and 1.0 mTorr O_2 (900 nm average thickness).

Figure 6 and Figure 7 show the influence of Cu-Sb ratio on percent transmission (at 12 µm) and conductivity, respectively, for films created in 0.5 mTorr O_2 and 1.0 mTorr O_2.

In terms of transmission, O_2 partial pressure highly influences the films properties while Cu-Sb ratio is a secondary effect that only appears when sufficient O_2 was present during synthesis. Interestingly, as Figure 6 shows, the highest percent transmission occurred when the Cu-Sb ratio was around 69:1 (dropping off when the ratio was either substantially increased or decreased).

In terms of conductivity, O_2 partial pressure had the opposite effect. This drop in conductivity is most likely the result of increasing oxidation. Films synthesized in 0.5 mTorr O_2 may have been only partially oxidized, while films synthesized in 1.0 mTorr O_2 were more fully oxidized; as the oxidation increased, the high conductivity metallic character was lessened.

Conclusions

- $Cu_xSb_yO_z$ shows IR-transparent conducting behavior when synthesized under appropriate conditions.
- Both transmission and conductivity are greatly influenced by O_2 partial pressure while sputtering. Increasing the O_2 partial pressure increases transmission and decreases conductivity.
- IR-Transmittance is exponential with respect to thickness. The absorption coefficient, β, of $Cu_{59}Sb_1O_x$ was found to be 162.63 cm^{-1}.

References

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