

SURFACE SCIENCE LETTERS

AUGER ELECTRON SPECTROSCOPY OF SURFACE CARBON ON Ag(110)

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The quantification of the amount of carbon present on a silver surface by means of Auger electron spectroscopy is complicated by the overlap of the carbon Auger signal with the silver $M_5N_1N_{4,5}$ emission at 266 eV [1,2]. It was previously assumed that the silver surface was free of carbon when the ratio of the 266 and 304 eV silver peaks measured in the differential, $dN(E)/dE$, mode was between 0.4 and 0.5. In recent studies of the oxidation of acetylene, ethylene, and ethane by atomic oxygen on Ag(110) it was found that carbon was quantitatively deposited on the silver surface at room temperature according to the following stoichiometry [3,4]



where $x = 2, 4$ or 6 for the different C_2 -hydrocarbons. Oxygen adsorption on the silver (110) surface produced a series of $(n \times 1)$ LEED patterns, and the maximum uptake yielded a $(2 \times 1)O$ LEED pattern that corresponded to a half monolayer of oxygen atoms [1]. The amount of carbon present on the silver surface was determined by combustion of the surface carbon with oxygen to carbon dioxide in temperature programmed experiments. This situation provided a method for the preparation of silver surfaces with known quantities of carbon up to a carbon density of 1 carbon/silver atom for calibration of the carbon Auger signals on Ag(110).

Differential, $dN(E)/dE$, Auger spectra are presented in fig. 1 for the clean silver surface, curve A, and a silver surface covered with a $1/2$ monolayer of carbon produced from the titration reaction of a (4×1) oxygen atom covered silver surface with acetylene, curve B. The differential Auger spectrum for the carbon covered surface did not differ considerably from that obtained for a clean surface although the absolute intensity of the signal decreased. The ratio of the 266 to 304 eV peaks *decreased* from 0.50 to 0.44 upon deposition onto the clean surface of a half monolayer of carbon.

This dilemma was resolved by collecting the Auger spectra as direct energy distributions, $N(E)$, by electron counting and subtracting the Auger spectrum of the

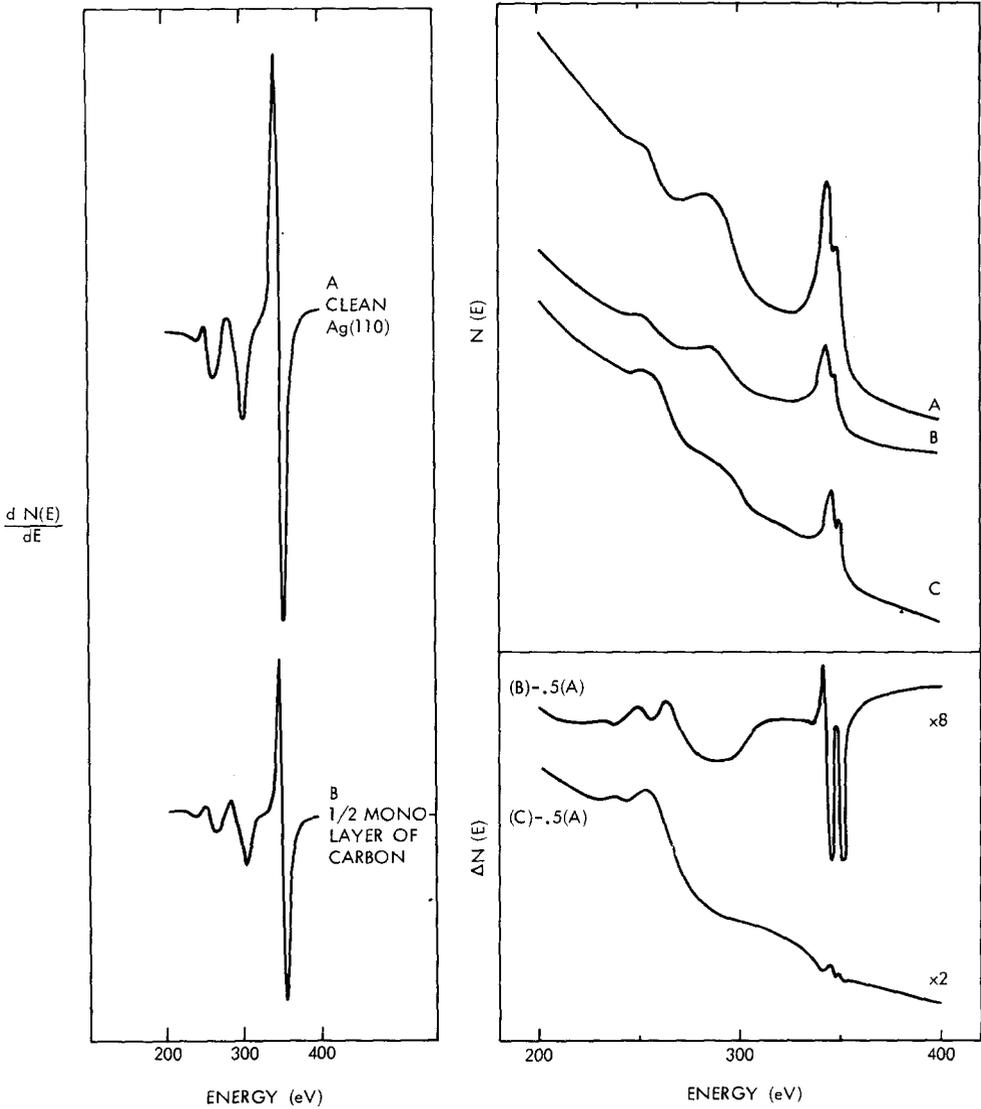


Fig. 1. Curve A, AES $dN(E)/dE$ of a clean silver (110) surface. Curve B, AES $dN(E)/dE$ after deposition of 4.2×10^{14} carbon atoms/cm². The spectra were obtained with 8 V modulation voltage and a 2.5 keV primary electron energy.

Fig. 2. Curve A, AES $N(E)$ of a clean silver (110) surface. Curve B, AES $N(E)$ after deposition of 4.2×10^{14} carbon atoms/cm². Curve C, AES $N(E)$ following 2×10^{-5} Torr s exposure to benzene at $T = 200$ K.

clean silver from that of the adsorbate covered surface. Fig. 2 contains direct energy distributions for the clean silver (110) surface, curve A, the half monolayer carbon covered surface, curve B, and for comparison a full chemisorbed monolayer of benzene at 200 K, curve C. Below these curves are the corresponding difference spectra for the direct energy distributions of the adsorbate covered surfaces produced by the subtraction of the clean silver signal. Note that attenuation of the silver Auger signal is compensated for in the subtraction. These difference spectra enable observation of the carbon Auger transitions. The Auger difference spectrum of the half monolayer of carbon produced via reaction (1), fig. 2, curve (B) – 0.5(A), possesses the three Auger peaks in the direct energy distribution at 236, 252 and 265 eV characteristic of a surface carbide [5]. Note the non-uniform attenuation of the silver Auger signal in the 350 eV energy range corresponding to a net shift to lower kinetic energy of the $M_{5}N_{4,5}N_{4,5}$ and $M_{4}N_{4,5}N_{4,5}$ transitions which is a consequence of carbide formation. The origin of the decrease in the $dN(E)/dE$ 266 to 304 eV ratio observed in fig. 1 is clarified from a comparison of curves A and B of fig. 2. The decrease occurred because the carbide Auger $N(E)$ features at 252 and 266 eV bracket the larger silver peak and produce a broader peak with a slight overall amplitude increase in this energy range. The slope of the resultant peak is not as steep and is responsible for the reduction of the 266 eV/304 eV ratio in the $dN(E)/dE$ mode.

The surface carbide Auger line shape was maintained upon heating to 425 K. Higher temperatures resulted in the loss of the sharp fine structure associated with the carbide but the total carbon signal remained constant in intensity. Parallel UPS measurements also exhibited major changes in the valence band region accompanying the Auger line shape change. The constant intensity of the carbon AES signal indicated that carbon did not diffuse into the bulk at elevated temperatures.

The amount of carbon deposited via reaction (1) is limited to carbon densities less than or equal to 1 carbon/silver atom and is dependent on the amount of atomic oxygen initially adsorbed. Therefore, for the purpose of an independent consistency check of the above quantification procedure, deposition of a known quantity of carbon by other means and at a carbon density greater than 1 carbon/silver atom is desirable. A monolayer of chemisorbed benzene satisfies these requirements. Photoemission measurements [6] indicate that a saturated chemisorbed layer of molecular benzene is produced following a 2×10^{-5} Torr s exposure of benzene to a silver (110) surface held at 200 K. The AES $N(E)$ spectrum for the benzene monolayer is presented in curve C of fig. 2, and below is the resultant curve following subtraction of the clean silver signal, labeled (C) – 0.5(A). The difference curve in this case shows a non-carbide line shape and only minor changes in silver emission over uniform attenuation. The corresponding $dN(E)/d(E)$ 266 eV/304 eV ratio is 1.25 for the monolayer of benzene, and is substantially above the clean surface value of 0.50.

The expected carbon densities of the two carbon covered surfaces presented in fig. 2 were estimated in the following manner for comparison with the integrated

areas of the carbon signals in the difference curves. A half monolayer of carbon on Ag(110) produced via reaction (1) corresponds to a density of 4.2×10^{14} carbon atoms per cm^2 . A full dense packed monolayer of benzene limited by its Van der Waals envelope (35.2 \AA^2 per molecule) implies a density of 2.8×10^{14} molecules per cm^2 or a density of 1.68×10^{15} carbon atoms per cm^2 . Therefore, the carbon Auger signal for the monolayer of benzene should be four times larger than that produced by the surface carbide in fig. 2. This is in agreement with the experimental observation since the carbide spectrum is presented on a scale four times more sensitive than benzene, and the integrated areas are comparable.

Although the presence of small quantities of carbon, less than 4.2×10^{14} atoms/ cm^2 , can not be confirmed by simple analysis of a low resolution $dN(E)/dE$ 266 eV/304 eV ratio such small carbon concentrations should produce a broadening of the 266 eV $dN(E)/dE$ peak on toward high kinetic energy. Recent analysis of the $dN(E)/dE$ peak widths indicated broadening of the 266 eV signal on a polycrystalline silver foil when a small quantity of carbon was suspect as a contaminant, but the 266 eV/304 eV ratio remained at 0.5 [7]. This broadening is also observed in the line shape from two different standard silver $dN(E)/dE$ Auger spectra presented in the Handbook of Auger Electron Spectroscopy [8,9]. The silver Auger spectrum obtained at 3 keV exhibits broadening of the 266 peak towards higher kinetic energy as well as oxygen contamination [8,9]. On the other hand, the silver Auger spectrum at 5 keV, apparently from a different sample, exhibits only minimal contamination and does not show broadening of the 266 eV peak [9]. Both samples are free of gross carbon contamination, but the sample whose Auger spectrum was collected at 3 keV exhibits Auger features which necessitates consideration of carbon contamination.

The present analysis of surface carbon on Ag(110) demonstrates that the difference curves of the direct Auger energy distributions enable reliable detection of Auger transitions attributable to carbon in the sub-monolayer concentration range. This approach was used to clarify the $dN(E)/dE$ Auger results that the $dN(E)/dE$ 266 eV/304 eV ratio initially decreases with increasing carbon concentration up to approximately 4.2×10^{14} atoms/ cm^2 (1 carbon/2 Ag atoms), and is well above the clean surface value at a carbon density of 1.68×10^{15} atoms/ cm^2 (2 carbons/Ag atom). The results also demonstrated that the surface carbide on Ag(110) was stable until 425 K and that surface carbon did not diffuse into the bulk at elevated temperatures.

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