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Adsorption of Sulfur on Bimetallic Surfaces:

Formation of Copper Sulfides on Pt(111) and Ru(001)

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ABSTRACT

The interaction of sulfur and copper on Pt(111) and Ru(001) has been examined using X-ray photoelectron spectroscopy (XPS) and thermal desorption mass spectroscopy (TDS). Cu/Pt(111) and Cu/Ru(001) surfaces were exposed to S_2 gas at 300 K. It was found that for both substrates stable copper-sulfide films were formed, of which the Cu-S/Ru(001) system was the more stable. The decomposition of the "Cu_2S" films on Pt(111) occurred at 600-850 K and on Ru(001) at 900-1000 K. Breakdown of the films led to evolution into the gas phase of sulfur (mainly as S_2) without desorption of copper or the sulfur chemisorbed on the substrate. This chemisorbed sulfur desorbed in a broad feature from 1000-1500 K. For the Ru(001) substrate the Cu atoms remained on the surface until they desorbed at 1080 K, while on Pt(111) the Cu atoms migrated into the Pt(111) surface to form a subsurface Cu-Pt alloy and no Cu desorption features were seen at temperatures as high as 1300 K. On Pt(111), copper-sulfide promoted the formation of a bulk-like platinum-sulfide. No sulfidation of ruthenium was detected in the presence of copper-sulfide films. For both substrates the sulfur atoms were found to highly perturb the copper sites, decreasing the ability of the noble-metal adatoms to adsorb CO.

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I. INTRODUCTION

It has been found that by making specific bimetallic systems (in this case a noble metal deposited on a transition metal surface) one can change the catalytic activity and selectivity of the metals for reactions that lead to the conversion of hydrocarbons.[1,2,3,4,5,6] A major problem associated with these catalysts is sulfur poisoning,[7] and for this reason, recently, we have been examining the effects of sulfur on the electronic, chemical and structural properties of bimetallic surfaces.[8,9] In this study, we examine the coadsorption of sulfur and copper on Ru(001) and Pt(111) surfaces using XPS and TDS.

Copper forms a strong chemisorption bond with Ru(001)[10,11,12] and Pt(111)[13,14] at room temperature. Cu atoms in contact with these substrates exhibit core levels shifted toward lower binding energy with respect to those of pure metallic copper.[11,13] This is a consequence of a charge redistribution in which Cu gains $3d$ electrons from the substrate but loses $4s,4p$ charge giving a small net charge transfer to the substrate. The overlap of the $3d$ electrons with the core electrons is much higher than that of the $4s,4p$ electrons therefore the Cu core levels are destabilized by electron-electron repulsion despite the small net charge transfer to the substrate.[15,16] At higher temperatures the behavior of Cu/Ru(001) and Cu/Pt(111) differ. As the temperature is increased Cu remains on the Ru(001) surface until it desorbs at ~1160 K for a monolayer coverage. For Cu/Pt(111), on the other hand, Cu migrates into the bulk of Pt at temperatures above 500 K, forming a subsurface Pt-Cu alloy.[13,14] No Cu desorption features are seen for temperatures as high as 1300 K.[13,14]

The behavior of sulfur on Ru(001)[17,18] and Pt(111)[19] is somewhat different. At temperatures between 300 and 600 K, the exposure of Ru(001) and Pt(111) surfaces to S_2 gas produces a

chemisorbed layer of sulfur without the formation of bulk sulfides.[9,17,19] The saturation coverage of S on Ru(001) is ~0.5 ML[17] while it is ~1.0 ML on Pt(111).[19] Sulfur desorbs from Ru in a broad peak from 1000-1500 K.[8,17] Sharp desorption features of S_2 and S are seen between 700 and 800 K for a Pt(111) surface with a high coverage of sulfur.[9] Low coverages desorb as a broad band from 1000-1500 K.[9,19]

II. EXPERIMENTAL

The experiments were carried out in an ultrahigh-vacuum system with a base pressure of less than 3×10^{-10} torr. The chamber was equipped with a quadrupole mass spectrometer for thermal desorption studies and a hemispherical electron analyzer with multichannel detection for photoemission studies. The photon source was unmonochromatized Mg Kα radiation. The total experimental resolution for the photoemission studies was approximately 0.8 eV. The electron detection was normal to the surface for the Ru(001) sample and 30° off-normal for the Pt(111) sample.

Both the Ru(001) and Pt(111) crystals were mounted on a manipulator capable of resistive heating to 1650 K and liquid nitrogen cooling to 80 K. The typical cleaning procedure for both crystals was cycling in 5×10^{-7} torr O_2, 600 to 1200 K several times followed by annealing to 1450 K in the case of Pt(111) and 1550 K in the case of Ru(001). Surface cleanliness was verified by means of photoelectron spectroscopy, and by obtaining the typical features expected for thermal desorption of oxygen. The copper was vapor-deposited on the Ru(001) and Pt(111) surfaces from a resistively heated W filament wrapped with high-purity Cu wire. Cu coverages were determined by TDS area analysis for the Ru(001) substrate,[12,20] and by measuring the CO uptake on free Pt sites for the Pt(111) substrate.[14b] A solid-state electrochemical cell (Pt/Ag/AgI/Ag_2S/Pt)[19,21] was used to vapor-deposit sulfur on the Ru(001) and Pt(111) surfaces. When a voltage is applied across the cell, sulfur evolved as S_n clusters (predominantly S_2).[21] Coverages of sulfur were determined by the intensity (area) of the sulfur photoelectron peak and referenced to a saturation coverage of 0.5 ML on Ru(001) at 500 K,[17] and 0.33 ML on Pt(111) at 750 K.[19] Coverages are reported with respect to the number of Ru(001) or Pt(111) surface atoms with one adatom per surface atom corresponding to $\theta=1$.

III. RESULTS AND DISCUSSION

III.1 Copper and Sulfur on Pt(111)

Figure 1 shows the photoemission results for annealed submonolayer Cu coverages on Pt(111), alone (Figure 1A), and a Pt(111) surface pre-treated with a saturation coverage of S (Figure 1B). Focussing on the top panel, we note a shift of 0.6 eV to lower binding energy for the submonolayer coverage of Cu as compared to bulk Cu at 340 K.[13] Upon annealing to temperatures above 500 K there is a further shift to lower binding energy (0.3 eV at 800 K) and a reduction in the Cu $2p_{3/2}$ peak intensity which is completely attenuated by 1200 K. This indicates migration of Cu into the bulk of Pt(111) with subsequent alloy formation.[13,14] No Cu desorption is detected in this temperature range.[14] On the S-pre-treated surface (bottom of Fig. 1) the initial binding energy position for the Cu $2p_{3/2}$ peak is 0.3 eV lower than that of bulk Cu, but is 0.3 eV higher than that of Cu atoms bonded to clean Pt(111). This indicates the formation of a copper-sulfide film.[18] Auger

Cu L_3VV data showed an even larger shifts in kinetic energy (~1 eV) between the Cu-alone and Cu-S/Pt(111) systems; also consistent with the formation of a copper-sulfide film.[18] Upon annealing we again notice a shift to lower binding energy (0.3 eV for 900 K) and a reduction in the Cu $2p_{3/2}$ intensity. This behavior indicates that the copper-sulfide film formed at 320 K decomposes at temperatures higher than 500 K with Cu migrating into the bulk of Pt.

Figure 2 shows thermal desorption results for a Cu-S/Pt(111) surface. The surface was prepared at 300 K and no desorption peak was observed below 600 K. In Figure 2, there is a strong desorption feature in the mass 64 signal centered at 710 K. A reduced intensity is present at the same temperature for mass 32 but that is mainly due to cracking of the S_2 species. The small signal present for mass 63 is a carry-over of the signal from mass 64. In all cases no strong signal is seen at other temperatures. For Cu/Pt(111) surfaces, Cu does not desorb at temperatures below 1300 K.[14]

In general, we found that Cu/Pt(111) (θ_{Cu}<4 ML) surfaces were able to adsorb significant amounts of sulfur at temperatures between 300 and 500 K. "Cu_2S" films supported on Pt(111) breakdown in the temperature range from 600 to 850 K (at 900 K, only a small amount of S, θ_S<0.4 ML, is left on the surface). In these cases, the "Cu_2S" films are not as stable as those formed on a Ru(001) substrate where breakdown and subsequent sulfur desorption do not occur until at least 900 K (see below). The desire for Cu to migrate into Pt (and form a Cu-Pt alloy) prevents formation of a stable copper-sulfide layer.

Figures 3 and 4 display photoemission results for two S/Cu/Pt(111) systems containing 3.8 and 0.41 ML of Cu, respectively. The figures show the Cu $2p_{3/2}$ (top) and Pt $4f$ (bottom) core levels as a function S_2 exposure, first at room temperature and subsequently at elevated temperatures from 500 to 550 K. In Figure 3A the Cu core levels shift to lower binding energy upon S_2 exposure and shift back upon annealing to 550 K. This indicates the formation of a Cu_xS film (x≈1) followed by transformation of this film into the more stable Cu_xS (x≈2).[18] During this process the Pt core levels show the emergence of a new feature at ~1.2 eV higher binding energy which dominates the spectrum after repeated exposure of S_2 at 550 K. This new peak indicates the formation of a platinum sulfide[22] (the alloying of Pt and Cu induces a maximum shift of only +0.4 eV in the Pt $4f_{7/2}$ level[13]). For the system containing 0.41 ML of Cu (Figure 4), a broadening of the Pt $4f$ core levels (to the higher binding energy side) is evident after S_2 exposure at 550 K. Annealing of S/Pt(111) surfaces to 600 K or exposing of Pt(111) to S_2 at 600 K did not produce an increase in the FWHM or position of the Pt $4f$ core levels.[9] Thus, it appears that the presence of copper promotes the formation of platinum sulfides. These sulfides decomposed at temperatures in the range between 700 and 800 K, producing S_2 gas, metallic Pt and chemisorbed sulfur.

Figure 5 shows the interaction of CO with a clean Pt(111) surface and a Cu/S/Pt(111) surface. In Figure 5A the O 1*s* spectra clearly shows two distinct CO species at 532.5 and 530.8 eV for clean Pt(111). This is in agreement with data reported in the literature.[23] The first peak corresponds to CO adsorbed into on top sites and the second to CO adsorbed into bridge sites. For the Cu/S/Pt(111) surface at 80 K a single, small CO feature is seen at 532.8 eV. Upon annealing to 175 K this feature disappears. On Cu/Pt(111), CO desorbs at temperatures between 260 and 500 K.[13,14] In Figure 5B the Cu $2p_{3/2}$ features for the Cu/S/Pt(111) sample are shown before and after CO adsorption at 80 K. A small shift of 0.1 eV to higher binding energy is seen after CO adsorption. In contrast, the adsorption of CO on Cu/Pt(111) surfaces induces a shift of ~+0.8 eV in the Cu $2p_{3/2}$ level.[13]

III.2 Copper and Sulfur on Ru(001)

Figure 6 shows the photoemission results for a S/Cu/Ru(001) system as a function of S coverage. In Figure 6A we see a shift of 0.4 eV to higher binding energy in the Cu $2p_{3/2}$ peaks as the sulfur coverage is increased to 0.38 ML. Further S adsorption shifts the Cu $2p_{3/2}$ level toward lower binding energy (0.5 eV for θ_S=1.35). The Cu L_3VV Auger, shown in Figure 6B, indicates a shift to lower kinetic energy upon S adsorption on the Cu/Ru(001) sample. The S $2p$ region, shown in Figure 6C, indicates a shift of the S $2p$ centroid to higher binding energy with increasing S coverage. All these trends are consistent with the formation of copper sulfides on Ru(001).[18] Upon initial S_2 exposure a low concentration copper-sulfide is formed, Cu_xS with $x \approx 2$, which is converted to Cu_xS with $x \approx 1$ at higher exposures.[18]

Figure 7 gives the TDS results for the aforementioned S/Cu/Ru(001) system. We note strong S_2 desorption features centered at temperatures of 400 and 950 K, which correspond to the decomposition of copper sulfides (probably Cu_xS ($x \approx 1$) at 400 K and Cu_xS ($x \approx 2$) at 950 K).[18] A Cu desorption feature is centered at 1080 K. The small features in both mass 63 (at 950 K) and mass 64 (1080 K) signals are due to cross-over from the signal of the other respective mass. XPS data taken after annealing to 1200 K during the thermal desorption experiments indicated that only a small amount of sulfur (~0.3 ML) was present on the surface. In the S/Cu/Ru(001) system of Figure 7, the bimetallic bond is weakened by the presence of S, and the Cu desorption temperature is ~90 K smaller than that seen on clean Ru(001) (~1160 K). Similar behavior has been seen for the coadsorption of S with Zn,[8b] Au,[8c] and Ag[8a] on Ru(001). In these systems, S and the admetal compete for the electrons of the Ru substrate, and this reduces the strength of the bimetallic bonds.[8]

Experiments similar to those displayed in Figures 3 and 4 for S/Cu/Pt(111) surfaces were also carried out for several S/Cu/Ru(001) systems. The Cu/Ru(001) surfaces were exposed to S_2 gas at 300 K to form films saturated with sulfur (Cu_xS, $x \approx 1$). Annealing of these Cu_xS/Ru(001) systems to temperatures between 600 and 800 K induced the reaction: $(2/x)\ Cu_xS_{film} \rightarrow Cu_2S_{film} + (2-x/2x)\ S_{2,gas}$, without the formation of a ruthenium sulfide. In all the cases, the FWHM and position of the Ru $3d_{5/2}$ peak were almost identical to those of clean Ru(001). Thus, in contrast to the case of S/Cu/Pt(111) surfaces, for S/Cu//Ru(001) surfaces we found no evidence for a copper-promoted sulfidation of the metal substrate, although RuS_2 is more stable than PtS_2.[24] However, the cohesive energy of ruthenium is higher than that of platinum,[25] and therefore there is a larger activation barrier to formation of RuS_2 as compared to PtS_2.

We investigated the adsorption of CO on Ru(001) surfaces with submonolayer coverages of copper and sulfur ($\theta_S + \theta_{Cu} < 1$ ML).[26] In general, we found that the formation of Cu-S and Ru-S bonds leads to a weakening in the Cu-CO bond. For example, when CO is adsorbed on a Ru(001) surface pre-covered by 0.6 ML of Cu at 100 K, a shift of ~+0.5 eV is observed in the Cu $2p_{3/2}$ peak,[11] and the Cu-bonded CO molecules desorb from the surface at ~235 K.[12b] In contrast, for adsorption of CO on a Ru(001) surface pre-covered by 0.68 ML of Cu and 0.19 ML of S, the CO-induced shift in the Cu $2p_{3/2}$ level is only +0.15 eV at 100 K, and no CO molecules are present on the Cu atoms after annealing to 175 K.[26]

IV. CONCLUSIONS

We have shown that copper-sulfide films can be formed on both Pt(111) and Ru(001) surfaces. The copper-sulfide films formed on Ru(001) are more stable than those formed on Pt(111). This is due to the stronger substrate-noble metal bond formed by Pt(111) with Cu, weakening Cu-S interactions, and favoring alloy formation at higher temperatures.

On Pt(111), the copper-sulfide films promote the sulfidation of platinum. No sulfidation of Ru was detected in the presence of copper-sulfide films.

For copper-sulfide films on Pt(111), despite the lesser thermal stability of the film, S still strongly reduces the ability of Cu to adsorb CO, similar to that observed for copper-sulfide films on Ru(001).

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FIGURE CAPTIONS

Figure 1: Cu $2p_{3/2}$ photoemission results for A) submonolayer coverage of Cu on Pt(111) and B) submonolayer coverages of Cu and S on Pt(111). In each case the surface was annealed to the indicated temperature before taking the spectrum.

Figure 2: TDS results (masses 32, 63, and 64) for submonolayer coverages of S and Cu on Pt(111). Heating rate =5 K/s.

Figure 3: Photoemission spectra of multilayer depositions of Cu and S on Pt(111). This system was annealed to 550 K and further exposed to S_2 at 550 K. Regions of interest are A) the Cu $2p_{3/2}$ region and B) the Pt $4f$ region.

Figure 4: Photoemission spectra of submonolayer depositions of Cu and S on Pt(111). This system was annealed to 500 K and further exposed to S_2 at 500 K. Regions of interest are A) the Cu $2p_{3/2}$ region and B) the Pt $4f$ region.

Figure 5: Comparison of A) O $1s$ region for CO/Pt(111) with CO/Cu/S/Pt(111) at 80 K and 175 K and B) Cu $2p_{3/2}$ region for Cu/S/Pt(111) and CO/Cu/S/Pt(111).

Figure 6: Photoemission results for a monolayer of Cu on Ru(001) as a function of increasing sulfur coverage focussing on A) Cu $2p_{3/2}$ region, B) Cu L_3VV Auger region, and C) S $2p$ region.

Figure 7: TDS results (masses 63 and 64) for a sulfur-saturated monolayer of Cu supported on Ru(001). The lines at 600 and 800 K indicate successive annealing steps. At these points Cu $2p_{3/2}$ XPS and Cu L_3VV Auger spectra were acquired and showed that copper was forming "Cu_2S" on the surface.[18] The vertical line at 1160 K indicates the desorption temperature of a Cu monolayer from clean Ru(001).

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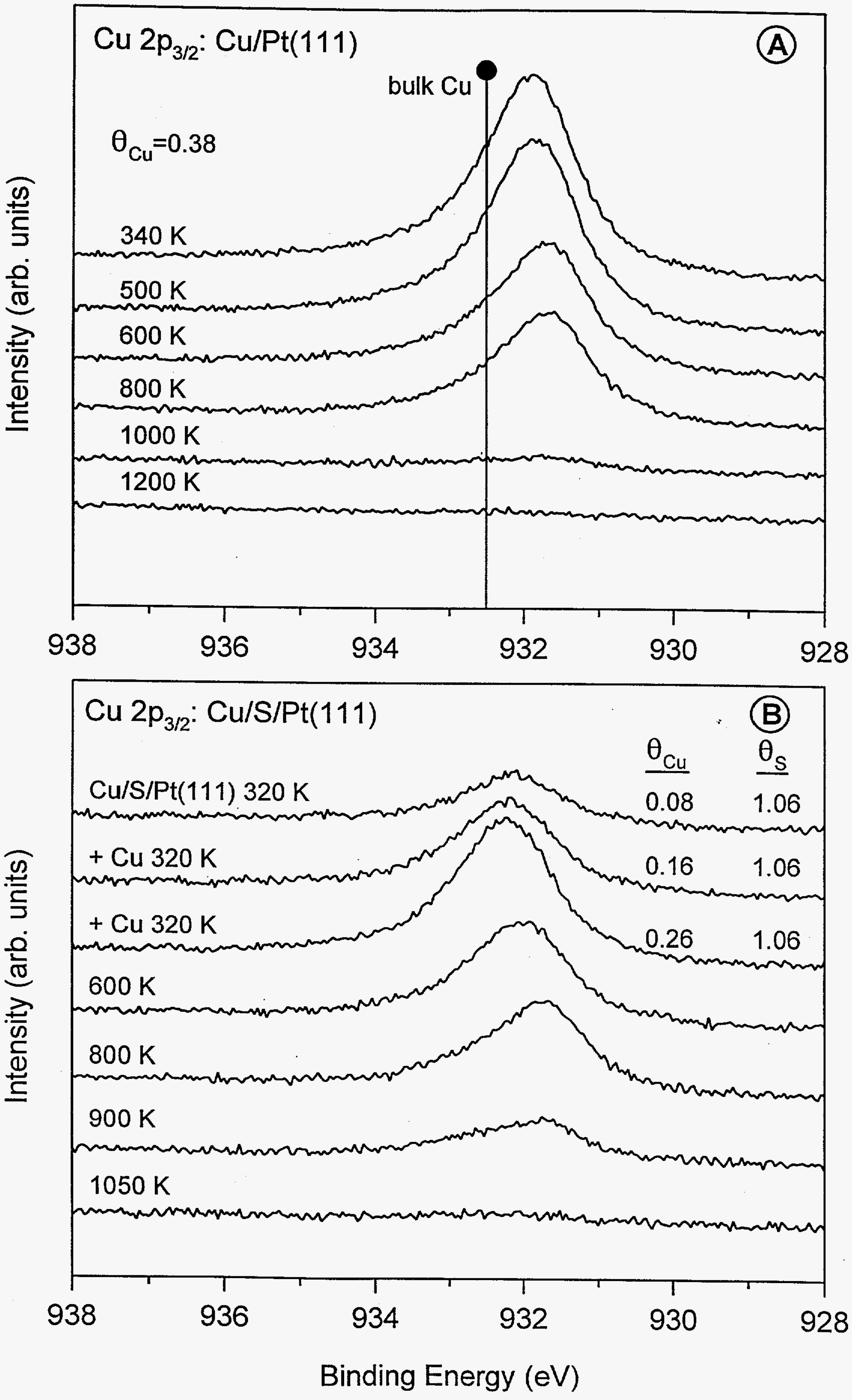
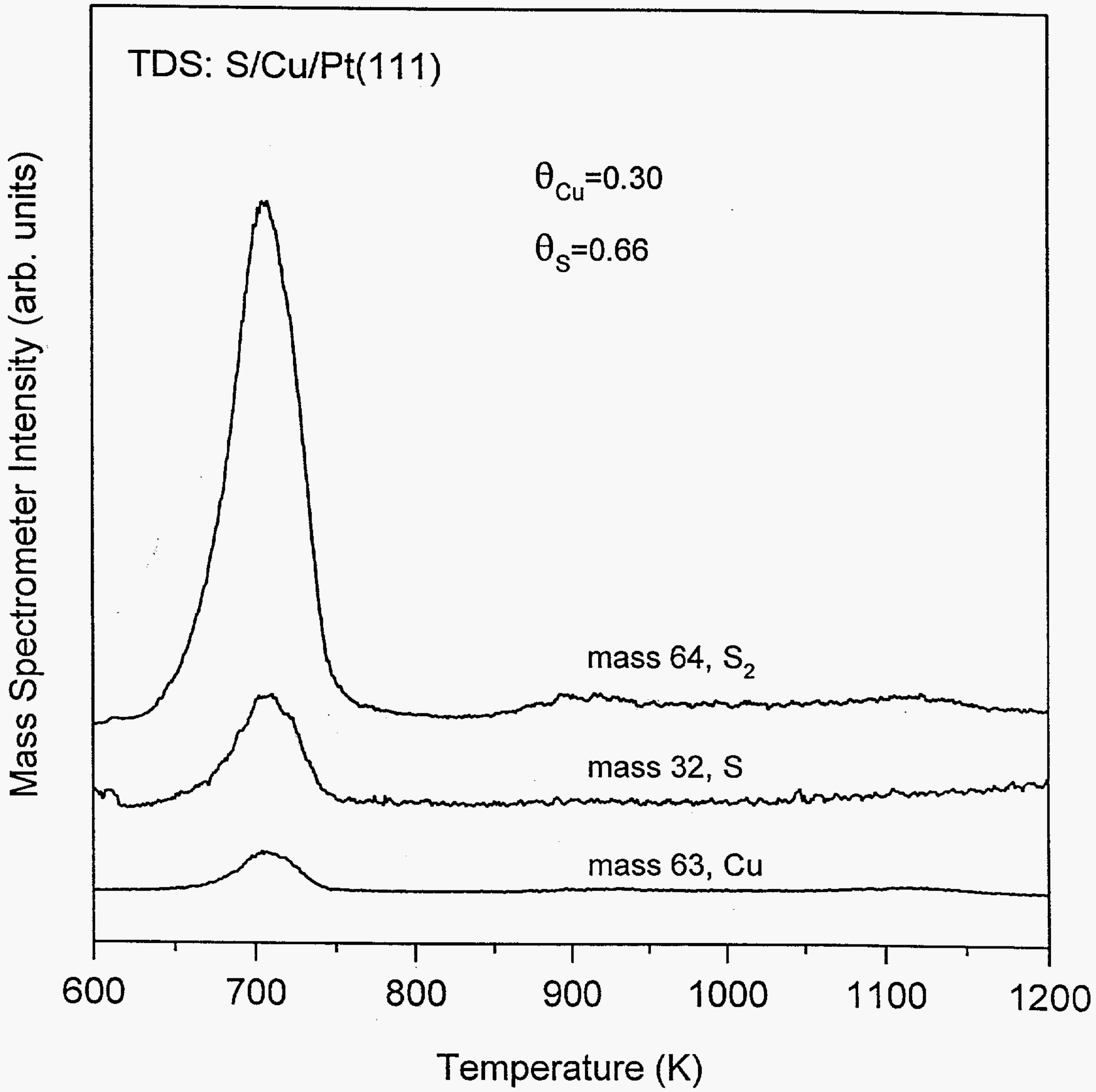


Fig. 1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θ_S=0.66
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mass 32, S
mass 63, Cu
Mass Spectrometer Intensity (arb. units)
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700
800
900
1000
1100
1200
Temperature (K)

Figure 2

ptcus1.spw

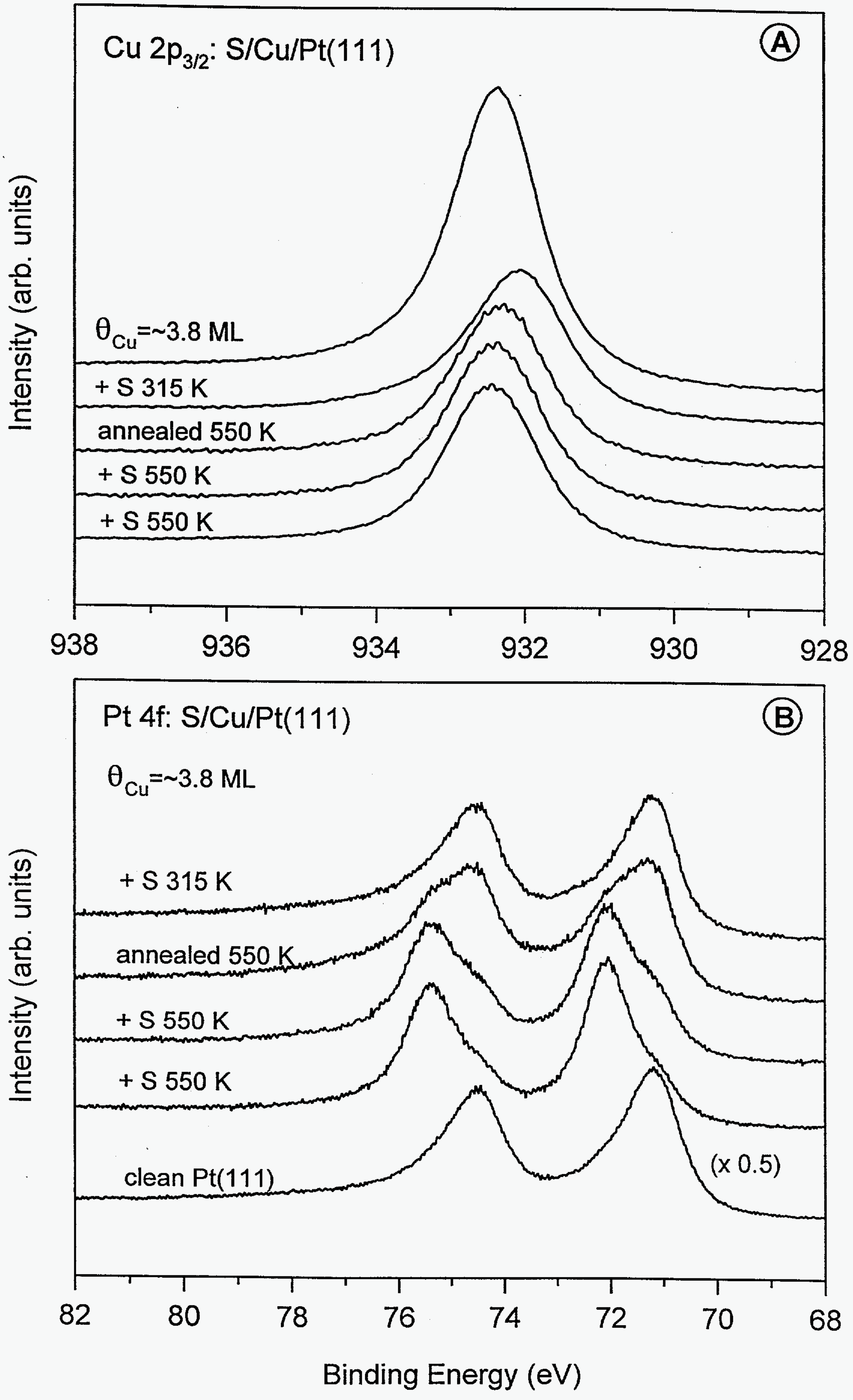

Fig. 3

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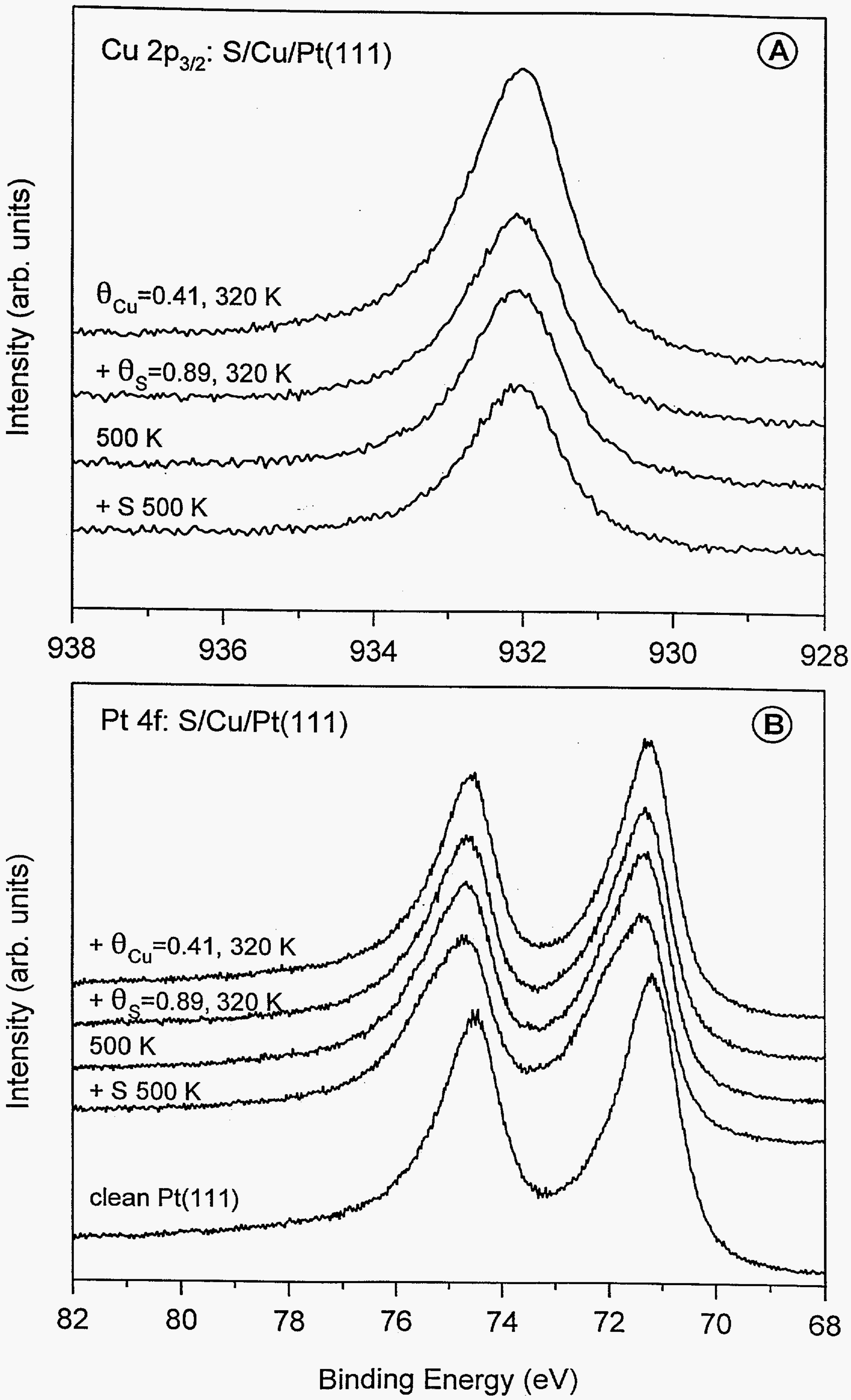

Fig. 4

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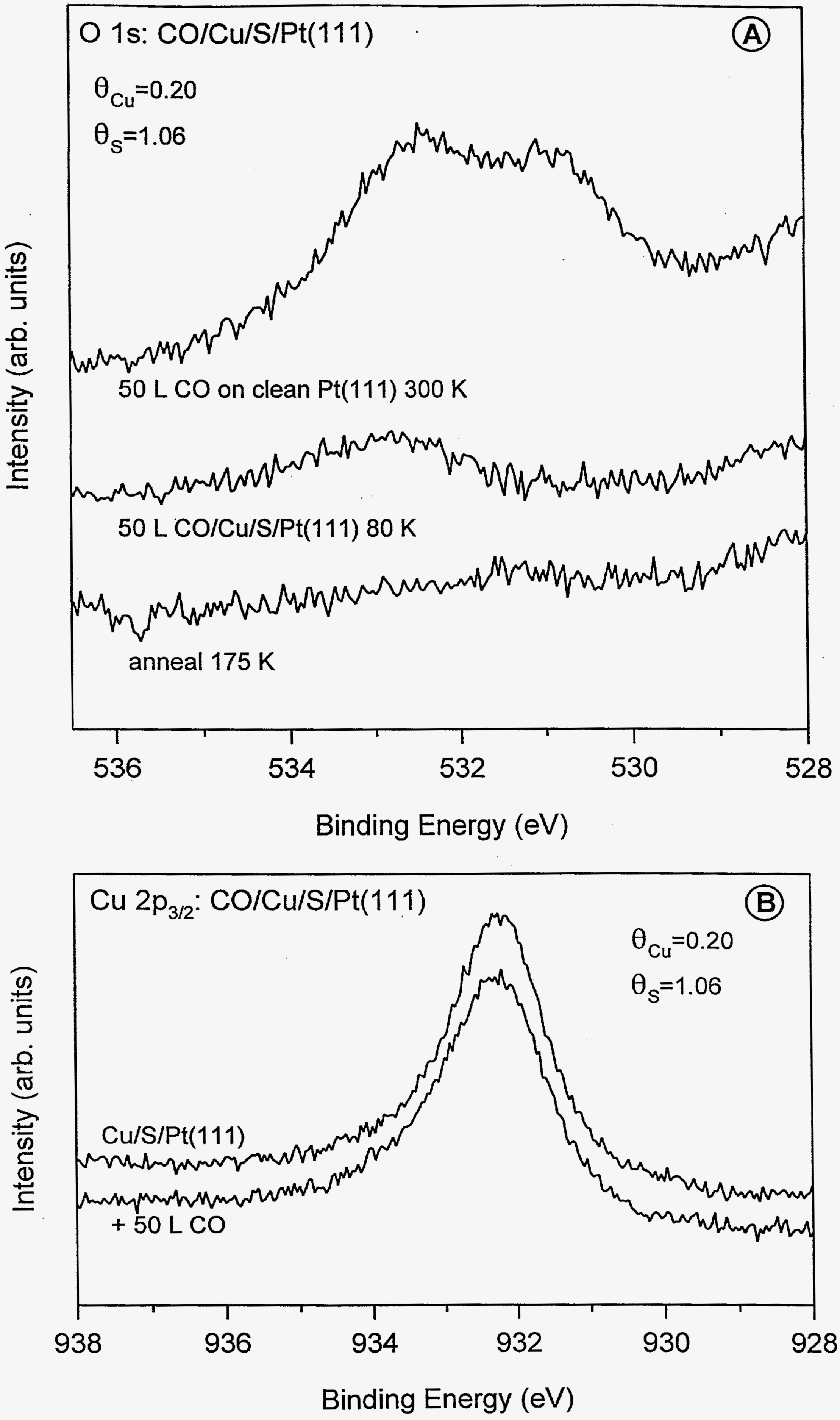

Figure 5

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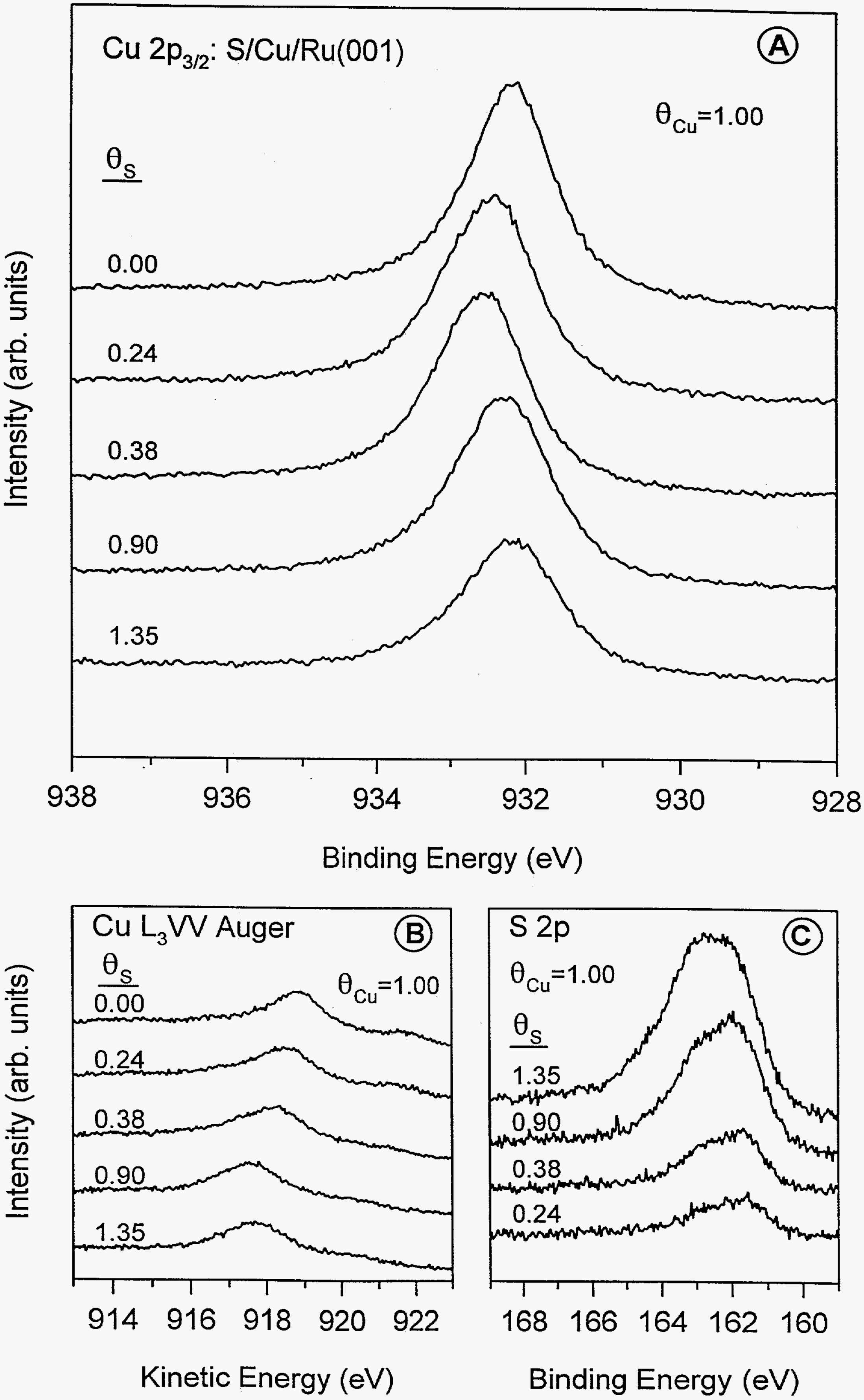

Fig. 6

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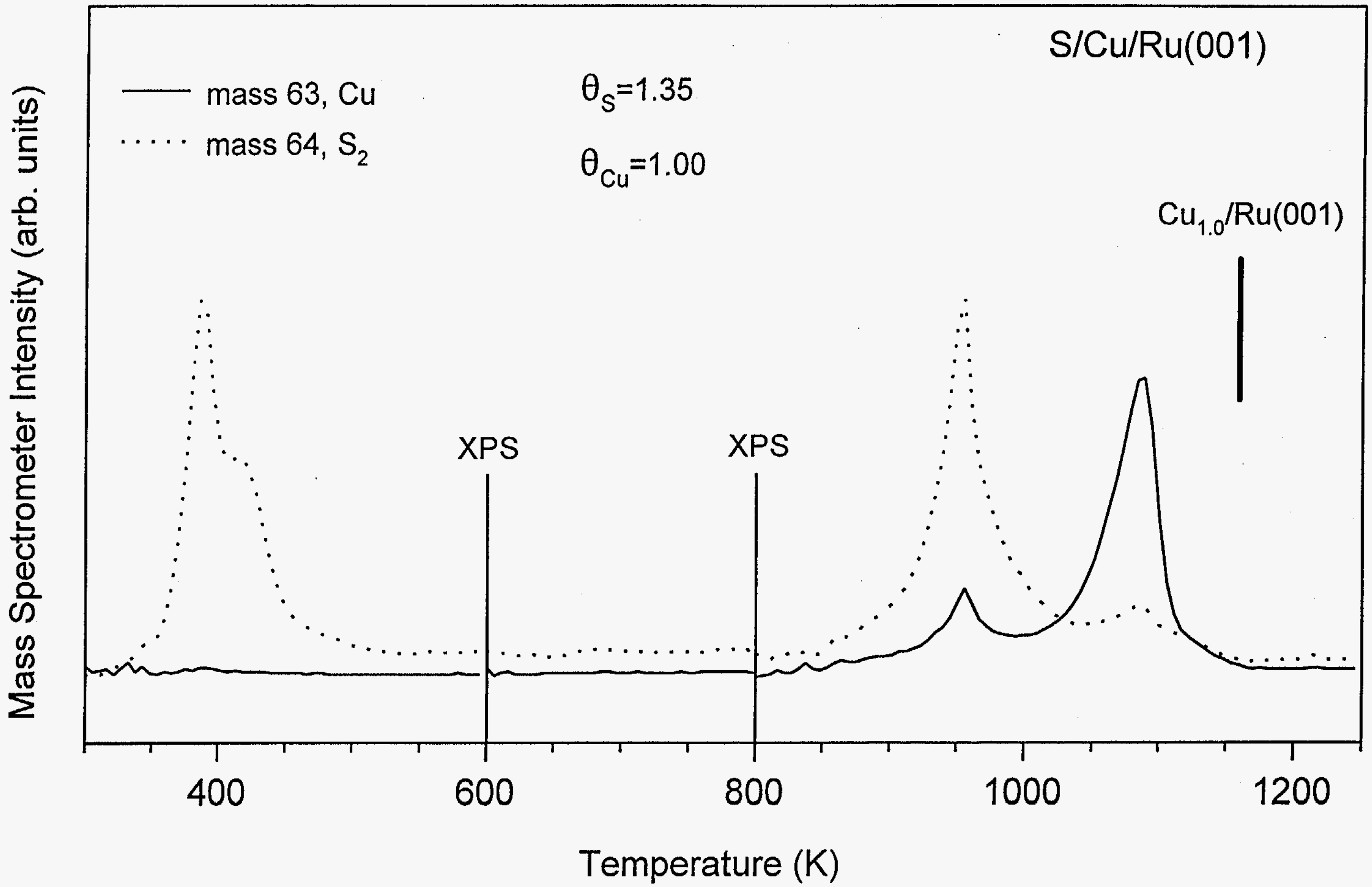

Figure 7