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TITLE ROTATIONALLY ANISOTROPIC SECOND-HARMONIC GENERATION STUDIES OF THE STRUCTURE AND ELECTRONIC PROPERTIES OF BIMETALLIC INTERFACES: Ag on Cu(110)

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Rotationally anisotropic second-harmonic generation studies of the structure and electronic properties of bimetallic interfaces: Ag on Cu(110)

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ABSTRACT

Rotationally anisotropic surface second-harmonic generation (SHG) has been measured from a clean, well-ordered Cu(110) single-crystal surface as a function of both surface temperature and Ag coverage. For the clean Cu(110) surface, the temperature dependence of the SH response at a fixed azimuthal angle can be correlated with a surface phase transformation. A large decrease in the rotationally anisotropic SH response as a function of surface temperature can be related to changes in the surface disorder. The results are compared with other studies of Cu(110) surface structure using both x-ray and He-atom scattering. The rotationally anisotropic SH response has also been measured as a function of Ag coverage with the Cu(110) surface temperature fixed at 300 K. The results closely follow the formation of an ordered Ag(111)-like overlayer, the nucleation of three-dimensional Ag nanoclusters (<20 Å thick) that enhance the anisotropic SH response, and the subsequent growth of a ~10 monolayer thick Ag film. Variations in the rotationally anisotropic SH response as a function of Ag coverage are used to separate the resonant surface electronic contributions to the nonlinear susceptibility of the interface.

1. INTRODUCTION

Interfaces play a key role in determining the mechanical, chemical, and electronic properties of materials. Obviously, the microscopic structure and thermal stability of interfaces are of fundamental importance in determining the suitability of a material for a particular application. New experimental methods capable of measuring interfacial properties are of great practical importance for materials studies of thin films, metals, semiconductors, and polymers. Purely optical methods have a unique and important role to play in interfacial studies since they allow the direct real-time interrogation of the structural and chemical environment of an interface over a variety of ambient experimental conditions ranging from liquids to ultrahigh vacuum (UHV). A number of recent experiments, performed under conditions ranging from UHV to electrochemical cells, have established that optical surface second-harmonic generation (SHG) can be an effective tool for surface and interface studies. [1,2] The technique is intrinsically interface specific since SHG is generally forbidden (in the electric-dipole approximation) by the inversion symmetry of bulk regions. A surface or interface between two dissimilar materials is, by definition, a non-centrosymmetric environment. Therefore, surface SHG is an allowed interface-specific process.

In the UHV environment, surface SHG has been used to probe *in situ* surface ordering and symmetry [3-6] and to follow changes in surface structure that occur on the picosecond time scale as a result of laser induced melting and recrystallization of surfaces. [7-10] Enhancements in the surface SH intensity can result from electronic resonance effects in the surface species. Such SH enhancements can be very sensitive to surface structure, the adsorption of adatoms, and the presence of 3-D surface structures, all of which can increase the second-order nonlinear susceptibility of the interface. [1,2]

Recently, we have been developing surface SHG for use in studying interfacial properties of clean, well-characterized single-crystal surfaces in the UHV environment. The present investigation of rotationally azimuthal SHG from clean Cu(110) and Ag overlayers on Cu(110) compliments our previous fixed azimuthal angle SHG experiments on the Ag/Cu(110) system. [11,12] The Cu(110) surface has C_{2v} symmetry, is highly corrugated, and consists of rows of Cu atoms separated by parallel troughs. It was anticipated from theoretical considerations [13] that the rotational anisotropy from the clean surface should have contributions arising predominately from two-fold symmetry elements in the surface second-order nonlinear susceptibility tensor. However, it was not known if changes in the rotationally anisotropic surface SH intensity would be observed as the surface temperature increased that could be correlated with presumed thermally induced changes in the surface structure. [14-16] In addition, changes in the rotationally anisotropic surface SH intensity could be expected resulting from the growth of an ordered Ag(111) overlayer on the Cu(110) substrate and, as indicated by our previous studies [11,12] of the Ag/Cu(110) system, the subsequent enhancement in SH intensity resulting from the growth of 3-D Ag nanoclusters (<10 monolayers thick) on the surface could significantly change the rotationally anisotropic SH response.

The experimental techniques used in this study combine optical surface SHG diagnostics with conventional UHV surface analysis techniques which include Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED). The Ag/Cu(110) system has been the subject of an extensive surface science investigation in our laboratory and therefore serves as an ideal model system for studying bimetallic overlayer growth using optical SHG techniques. [17,18]

2. EXPERIMENTAL

A bakeable UHV surface science chamber (base pressure $<2\times10^{-10}$ torr) equipped with instruments for making AES and LEED surface measurements was used for the rotationally anisotropic surface SHG experiments as shown schematically in Figure 1. A Cu single crystal (>99.995% purity) approximately 9 mm in diameter was cut and oriented to within $1/2^{o}$ of the (110) surface using x-ray diffraction techniques. The sample was mechanically polished to an optically flat mirror finish, electropolished, and mounted on a five-axis manipulator system that allowed heating, cooling, and azimuthal rotation over a range of $\sim220^{o}$. The Cu surface could be heated to 1000 K and cooled to ~170 K as measured by two thermocouples attached to different sample locations. The surface temperature measurements are accurate to within 5 K. Windows on the vacuum system allow for laser beam access to the sample face and for the specularly reflected SH laser beam to exit the chamber. The Cu surface was cleaned by repeated argon-ion sputtering followed by annealing in UHV for five minutes at 875 K. The surface was always cleaned and checked for impurities using AES prior to SHG measurements and a sharp LEED pattern was confirmed. LEED measurements also allowed a direct determination of the absolute surface azimuthal orientation to within $\pm 3^{o}$. Both AES and LEED were used to monitor the Ag coverage and overlayer growth morphologies and the results are described in detail elsewhere. [17,18] A collimated Ag vapor source operated at 1075 K and equipped with a manual shutter was used for controlled Ag depositions at a rate equivalent to approximately one Ag(111) monolayer (ML) per minute.

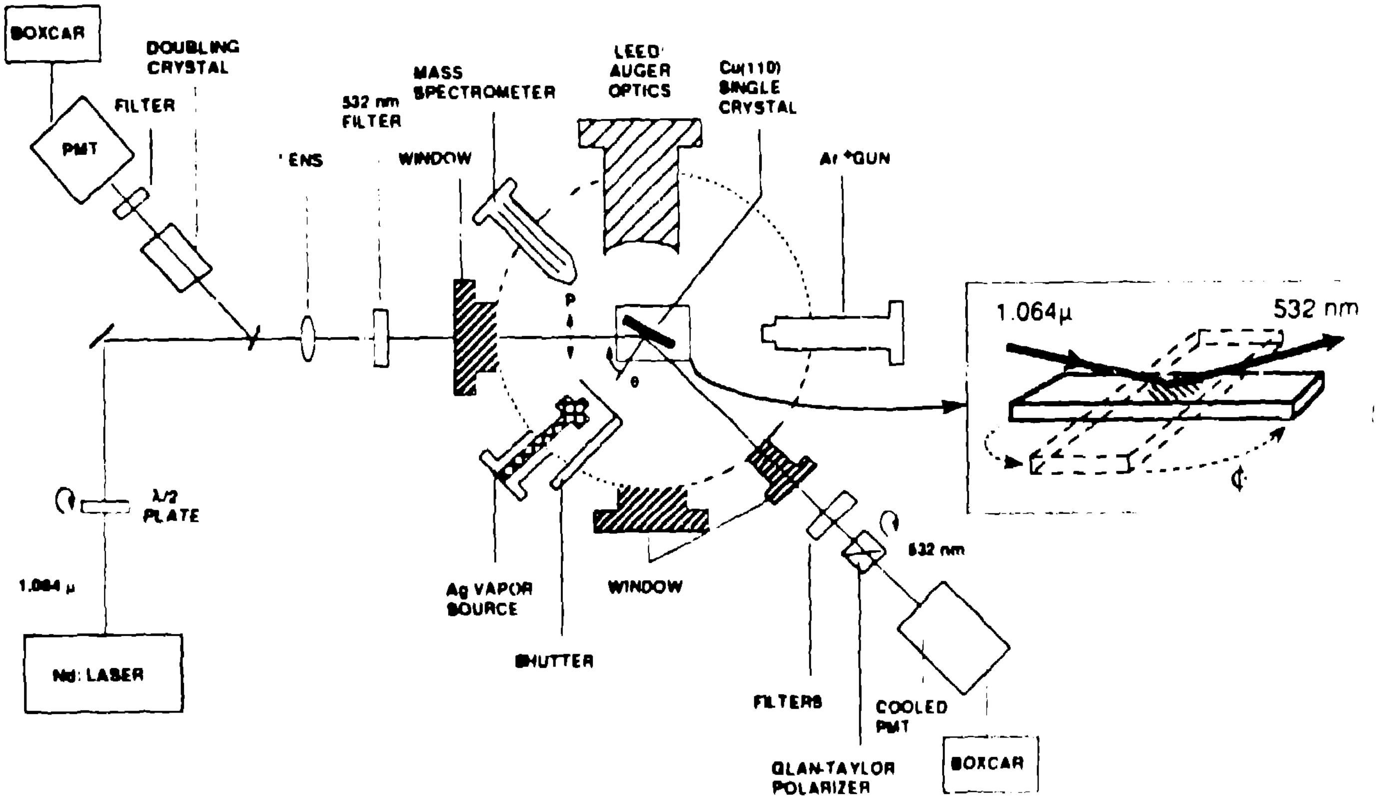

Figure 1. Apparatus for rotationally anisotropic surface SHG measurements with UHV surface science diagnostics. Details regarding the sample azimuthal rotation are shown in the expanded view.

All of the SHG measurements were made using a 10 Hz pulsed Nd:YAG laser at 1064 nm that provided pulses with ~10 nsec temporal width and pulse energies on the Cu surface of ~10 mJ (~10^{17} photons/pulse). The laser was mildly focussed onto the surface (spot size ~3 mm in diameter) at an incident angle of ~68° relative to the Cu surface normal. The laser polarization could be varied to select either p- or s-input polarization relative to the surface normal. Laser-induced surface damage or surface processes driven by laser heating were not expected since these laser fluences are a hundred times smaller than the laser damage threshold for Cu and Ag surfaces [19] and the calculated laser-induced surface heating [20] yields a surface temperature rise of <30°C.

The specularly reflected SHG output at 532 nm (>1000 photons/pulse) was separated from the fundamental with a combination of color filters, passed through a polarizer that could be rotated to pass only the p- or s-polarized component, and detected using a photomultiplier tube. A gated boxcar integrator and microcomputer were used to measure the output signal which was then normalized to the square of the incident laser power measured on a shot-to-shot basis by doubling in a KDP crystal. The microcomputer was also used to control other experimental aspects and for data analysis. Typically, the SH signal was detected in real-time as the substrate was automatically rotated over a fixed range of azimuthal angles (approximately -110° to 100° with respect to the rows of Cu surface atoms) with the substrate temperature held constant to within 2 K. In all cases, the linear reflectivity at 532 nm was measured over the same angle range and found to be constant to within 2% prior the measurements of the rotationally anisotropic SH intensity.

3. RESULTS

The rotationally anisotropic surface SHG experimental results described below focus on the temperature dependence of the SH response from clean Cu(110) and the changes in the SH response that occur as the result of the growth of Ag overlayers on the Cu(110) substrate. The results clearly demonstrate the selectivity and sensitivity of the optical SHG technique to changes in the surface structure and symmetry. These changes are then related to other studies of the thermal properties of the Cu(110) surface and the overlayer growth morphologies important in the Ag/Cu(110) system.

3.1. Rotationally Anisotropic SHG from Cu(110): Temperature Dependence

The dynamics of order-disorder transitions on surfaces have recently received considerable attention in the scientific literature since such processes can impose fundamental limits on material performance at elevated temperatures. Many high-index (11n) faces (where n>2) of single-crystal metal surfaces are known to undergo this type of phase-transition. By definition, roughening of an atomically clean surface consists of the proliferation of atomic steps by thermal means at a roughening temperature, T_R, where the surface free energy for creation of a step becomes zero. An unresolved question of fundamental importance is whether the roughening temperature of a low-index (110) surface can be lower than the bulk crystal melting temperature. For high index faces, a less stringent definition of roughening involving the proliferation of kinks on the already present step rows that can meander randomly has been suggested. The energy required for creation of a kink atom is lower than that required for generation of a step atom, thus roughening at temperatures lower than the bulk melting temperature can occur for stepped surfaces as opposed to low-index surfaces. Previous investigations have indeed shown both theoretically and experimentally that high-index faces of Cu, Ni, and other metals undergo a roughening transition well below the bulk melting temperature. [14]

Various surface-probe techniques have shown that the low-index Cu(110) face has an anomalous thermal behavior revealing a dramatic decrease in measured signal as the surface temperature is raised above ~500 K. Recent x-ray scattering data suggest that the Cu(110) surface undergoes a distinct thermal roughening transition at temperatures above ~600 K. [15] A sharp decrease in the scattered x-ray intensity above ~600 K was attributed to the migration of steps on the surface that form randomly shaped islands. However, very recently an energy-resolved He-atom scattering experiment found no evidence for the proliferation of steps up to 900 K. [16] While the He-scattered intensity falls rapidly above ~550 K as in the x-ray scattering experiments, an increase in the number of surface steps that would be manifest by a broadening in the angular distribution of the He-atom beam was not observed. The results suggest that, rather than Cu(110) undergoing an order-disorder transition, the surface has an increased vibrational anharmonicity above ~550 K due to an anomalous increase in the mean-square displacement of the surface atoms.

Our experiments have examined the thermal behavior of Cu(110) using rotationally azimuthal SHG. Owing to the inherent surface specificity of SHG, details regarding the temperature dependent surface structure and symmetry can be measured. In Figure 2 the SH intensity at fixed azimuthal angles of 0° and ~75° is shown as a function of the surface temperature. The projections of the input laser polarization relative to the azimuthal angles of the Cu(110) substrate correspond to 0° for p-polarization along the rows of Cu surface atoms in the [1$\underline{1}$0] direction and ±90° for p-polarization across the rows in the [00$\underline{1}$] direction. In all of the rotationally anisotropic SHG experiments reported below, no polarization selection of the SH output signal was performed. Polarization studies reported elsewhere [11,12] indicated that the s-polarized SH signal is a factor of ~30 smaller than the p-polarized SH signal. Therefore, with no polarization analysis of the SH output signal in the present experiments, we are assured the detected SH signal is predominantly p-polarized.

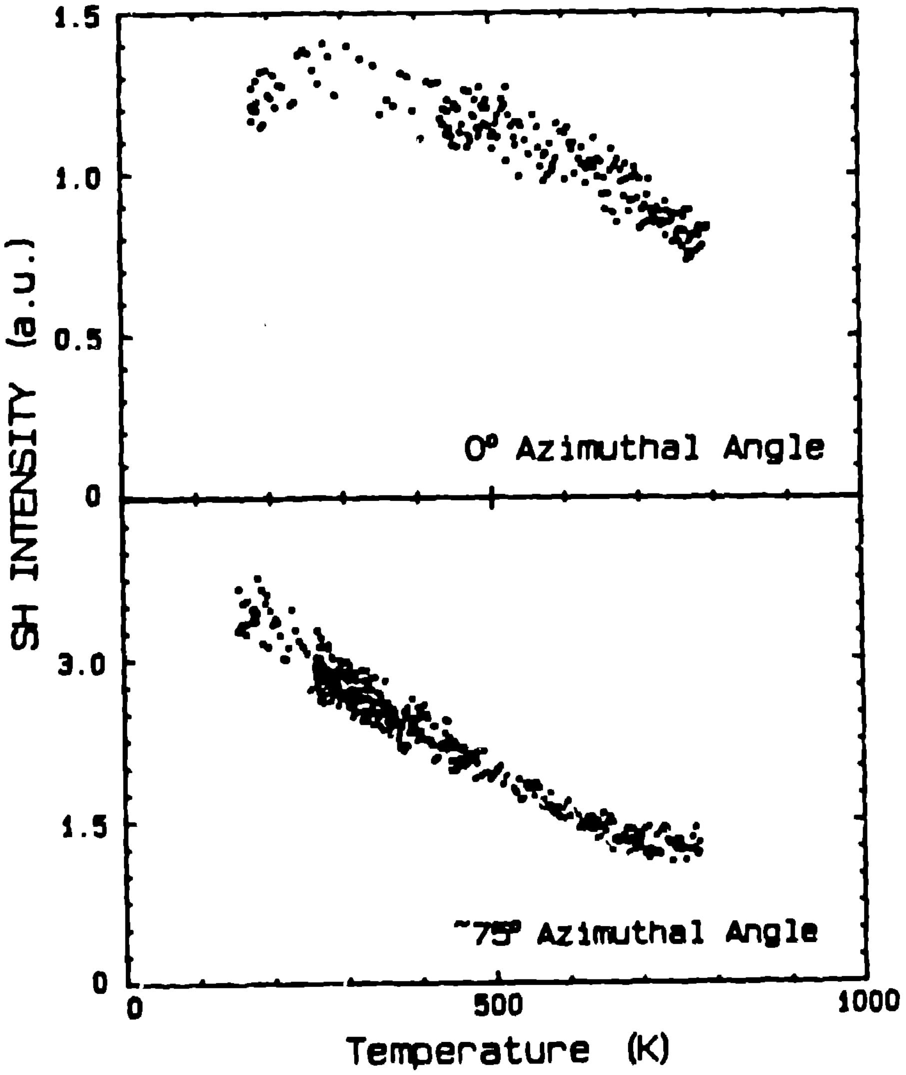

Figure 2. SH intensity as a function of Cu(110) surface temperature at fixed substrate azimuthal angles of 0° and 75° with respect to the rows of surface Cu atoms.

A smooth nearly linear decrease in the SH intensity is observed at 0° azimuthal angle up to ~500 K after which the SH intensity starts to decrease rapidly with increasing temperature. This observed thermal behavior very closely matches both the x-ray scattered intensity [15] and the He-scattered intensity [16] as functions of surface temperature. At an azimuthal angle of ~75° a sharp linear decrease in the SH intensity is observed up to ~700 K above which the SH intensity stops decreasing and remains constant. The temperature dependent behavior observed in Figure 2 is completely reversible as the surface temperature is ramped up and down. Extensive checks were performed to see if the possibility of impurities segregating from the bulk could affect the SH signals and none were found. Thus the temperature dependent SH intensity observed in Figure 2 could be used to monitor the surface temperature rise following heating from other sources. This type of measurement has recently been reported for the clean Ag(110) surface where the time dependent surface temperature was measured following heating induced by a pulsed laser. [21]

In Figure 3 the rotationally anisotropic SH intensity as a function of substrate azimuthal angle at eight different fixed surface temperatures is shown. Except for changes in the surface temperature, all other experimental conditions were fixed between individual azimuthal angle scans. Thus, the SH intensity at different temperatures and different angles can be directly compared on an absolute scale. At the lower temperatures a large degree of anisotropy in the SH intensity is observed with a distinct minimum near 0^0 and a maximum at ± 90^0.

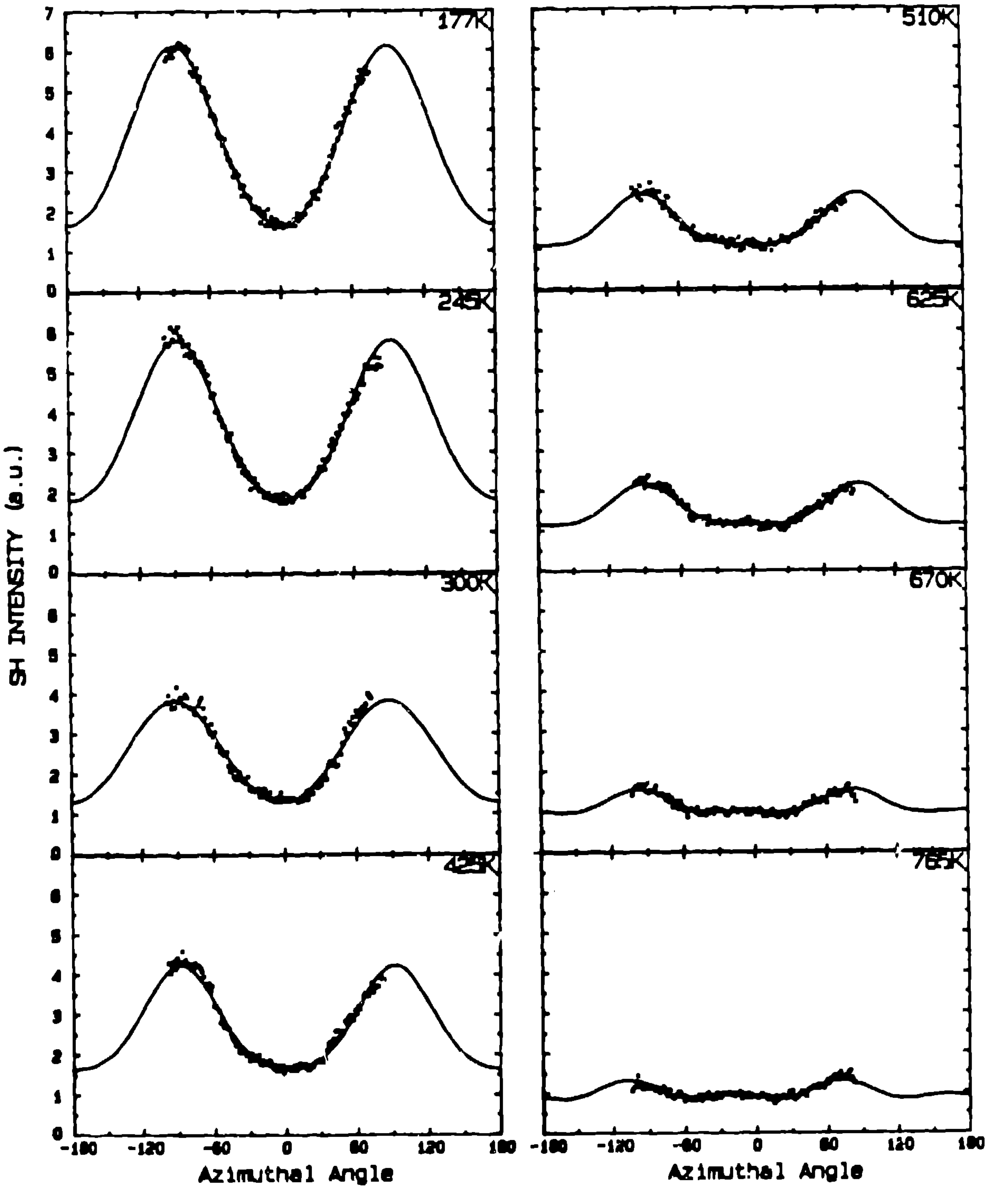

Figure 3. Rotationally azimuthal SH intensity as a function of Cu(110) surface azimuthal angle at the fixed surface temperatures indicated. The solid lines are theoretical fits to the data discussed in the text.

The solid lines in Figure 3 are theoretical fits [13] to the data using an expression for the SH intensity as a function of the azimuthal angle, ϕ, of the form

$$I_{SH} = \mid A + B\cos(n\phi) + C\cos(n\phi) \mid^2 \qquad (1)$$

where the coefficients A, B, and C represent the isotropic, n-fold anisotropic, and 2n-fold anisotropic susceptibility elements, respectively. For the clean Cu(110) surface, n=2 since the surface has two-fold C_{2v} symmetry. It can easily be seen from Figure 3 that the rotationally azimuthal SH intensity undergoes a rather dramatic decrease with increasing surface temperature. For the 177 K surface a very pronounced anisotropic two-fold SH response is observed superimposed on an isotropic background where $B/A = -0.32$ and $C = 0$. As the surface temperature is increased the anisotropic two-fold contribution to the SH intensity is observed to decrease significantly and a small decrease in the isotropic contribution is observed. For example, at 300 K $B/A = -0.27$ and $C \sim 0$. At 765 K the anisotropy responsible for the oscillatory changes in SH intensity has nearly vanished, $B/A = -0.085$, and a significant four-fold coefficient $C/A = 0.063$ is needed to adequately represent the data. Such a pronounced decrease in the anisotropic coefficients would be expected if the two-fold symmetry of the Cu(110) surface disappeared due to thermally induced "roughening" effects.

In a separate experiment, the clean Cu(110) surface held at 300 K was sputtered using 3.0 keV Ar^+ (five minutes at ~20 μA). LEED measurements performed following sputtering indicated a very diffuse background with almost no evidence of surface order. The rotationally anisotropic SH response at 300 K was measured under identical conditions to those described above and found to be nearly identical to the data shown in Figure 3 at 765 K (i.e. $B/A = -0.071$). This result implies that the deliberately disordered sputtered Cu surface and the Cu(110) surface at 765 K have similar overall structures. Such would be expected if a thermally induced surface phase transition occurred resulting in a significant degree of surface disorder.

With s-input laser polarization and the surface temperature fixed at 300 K, the rotational anisotropic SH intensity was measured as a function of azimuthal angle. Using the same input laser pulse energy and identical geometry as that used to obtain the data in Figure 3, the observed SH intensity was approximately 30 times weaker than the 300 K data shown in Figure 3. A clearly defined maximum was observed in the SH intensity at 0^0 and a minimum at $\pm 90^0$. Fits to the data yield $B/A = 0.071$ and $C/A = 0.051$, indicating a significant four-fold coefficient is required to represent the data. It is worth noting that for either p- or s-input polarization the rotationally anisotropic SH intensity is observed to maximize when the projection of the incident radiation polarization lies across the rows of Cu surface atoms.

3.2. Rotationally Anisotropic SHG from Ag on Cu(110): Ag coverage Dependence

The sensitivity of SHG to surface structure and symmetry make it possible to investigate detailed properties regarding the growth, structure, and stability of ultra-thin films. However, very few SHG studies of metal overlayer growth in the UHV environment have appeared in the literature.[2] The present study is intended to provide information regarding changes in overlayer structure and symmetry in the Ag/Cu(110) system. Part of our interest in studying the Ag/Cu system was in separating contributions to the SH response resulting from either changes in surface structure or changes in the free electron, interband electron, or surface-state electronic resonance effects.

Our previous studies of Ag overlayer growth on Cu(110) at 300 K using AES, LEED, and Rutherford backscattering spectroscopy [17,18] have shown that at submonolayer coverages, Ag was found to grow in the troughs on the Cu surface. The first one monolayer thick Ag adatom layer forms an ordered, commensurate Ag(111) hexagonally close packed overlayer with the Ag-Ag nearest neighbor distance aligned across the Cu troughs. This Ag(111) overlayer gives rise to a sharp c(2x4) LEED pattern. Additional Ag deposition, between one and two monolayers, results in the nucleation of 3-D Ag clusters ~8 layers thick (~20 Å tall) on top of the Ag(111) monolayer template. With further Ag deposition, the Ag clusters were found to grow across the surface and coalesce to form a continuous but disordered Ag film.

The SH intensity detected at a fixed azimuthal angle was observed to undergo changes as Ag was deposited on Cu(110) at 300 K.[11,12] The SH intensity initially decreases for the first ~0.5 ML of Ag deposition and then recovers to near its initial value at ~1.0 ML. Between 1.0 and 1.5 ML, the SHG intensity increases above the clean Cu(110) signal level by a factor of approximately three, and then decays smoothly above ~1.5 ML to a constant value at ~9 ML similar to SHG from bulk Ag. The initial decrease in the SH intensity is attributed to changes in the interband electronic resonance contributions. Cu has a 3d-4s interband electronic transitions lying between 2.0 and 3.0 eV. Ag has no optical transitions below ~3.6 eV [22]. The Cu-vacuum interface is therefore expected to have resonantly enhanced SHG contributions at 532nm (2.34 eV).

The pronounced enhancement of the SH signal only occurs at Ag coverages where 3-D Ag nanoclusters are known to nucleate and grow. The efficiency of SHG from the interface is mediated by the presence of 3-D Ag nanoclusters that couple the radiation field into excitation of surface plasmons as confirmed by polarization studies. Between 1.5 and ~9 ML the SH signal decay corresponds to Ag nanoclusters growing across the surface and eventually coalescing to form a continuous Ag film. At different fixed azimuthal angles the coverage dependencies of the SH intensity show very similar features to those just described. However, the absolute intensity of the SH signal is a strong function of the azimuthal angle. Of principle concern in this study is whether changes in the rotationally anisotropic SH response for different Cu and Ag overlayer structures can account for the observed SH intensity changes as a function of Ag coverage at fixed azimuthal angles. [11,12]

The rotationally anisotropic SH intensity measured at 300 K as a function of substrate azimuthal angle at seven different Ag overlayer coverages is shown in Figure 4. As for the clean Cu(110) results discussed above, no changes in the experimental setup were made between individual azimuthal angle scans except for the deposition of a known amount of Ag. Thus the SH intensities can be compared on an absolute scale. The solid lines in Figure 4 are theoretical fits [13] to the data using an expression similar to Equation 1 for the SH intensity as a function of the azimuthal angle

$$I_{SH} = | A + B\cos(2\phi) + C\cos(4\phi) + D\cos(3\phi) + E\cos(6\phi) |^2 \qquad (2)$$

where the coefficients A, B, and C, are defined in Equation 1 for the Cu(110) surface and the coefficients D and E represent possible three- and six-fold anisotropic susceptibility contributions derived from the hexagonal Ag(111) overlayer template having C_{3v} symmetry that is present on top of the Cu(110) surface at Ag coverages above ~1 ML.

Large changes in the overall SH intensity and concurrent changes in the shape of the anisotropy as a function of azimuthal angle are observed with increasing Ag coverage. As described in conjunction with Figure 3, the 300 K clean surface has a very pronounced anisotropic two-fold SH response. At coverages of 0.5 ML, where the Ag resides in the Cu(110) troughs, and 1.0 ML, where a Ag(111) hexagonal overlayer is formed, the anisotropic SH response is virtually unchanged except for a small decrease in the isotropic background. At 1.5 ML coverage, where 3-D Ag nanoclusters have nucleated on the surface, the overall rotationally azimuthal SH intensity increases by a factor of nearly three over the clean Cu(110) values and a significant change in shape of the anisotropic SH response is observed. The fit to the data using Equation 2 requires a significant two-fold coefficient *and* a three-fold coefficient (B/A=-0.37, D/A=-0.11, C=0, and E=0) to adequately represent the data. It is impossible to fit the data using Equation 1 with either n=2 or n=3 symmetry elements exclusively. As the surface coverage is further increased from 1.5 ML to 9.0 ML, where Ag nanoclusters coalesce to form a uniform though disordered Ag film, the anisotropic SH intensity is observed to decrease smoothly until at 9.0 ML the anisotropic SH intensity has been nearly erased. Fits to the data over this coverage range again require two- and three-fold coefficients to adequately represent the data, and at the higher coverages a significant change in the azimuthal angle offset is also required. For example, an azimuthal angle offset of ~15° is required to fit the data at 9.0 ML. This offset may be indicative of changes in the absolute azimuthal orientation of the thick Ag film relative to the substrate.

4. DISCUSSION

While the SHG experiments described above cannot uniquely resolve the debate concerning the temperature induced dynamics of the Cu(110) surface with regard to the presence of a "true" order-disorder transition [15] or an anomalous vibrational anharmonicity [16], it is worth noting some distinct differences intrinsic in the experimental techniques employed. First, consider the interaction times inherent in surface structural probes based on x-ray scattering [15], He-atom scattering [16], and the present study using optical SHG. X-ray scattering predominantly involves the interaction of incident x-rays with the core electrons of near surface atoms. Such an interaction can be viewed as an instantaneous event involving an interaction time of $<10^{-15}$ sec. Optical SHG involves the scattering of an incident photon from either the free or interband electrons of the surface atoms. The intensity of the SH signal is determined by the nonlinear susceptibility of the surface atoms which is in turn related to their nonlinear polarizability. The interaction time involved can again be viewed as instantaneous typically lasting $<10^{-15}$ sec. However, for He-atom scattering the interaction time with the surface atoms is different. In the He-atom scattering experiments reported above [16] the He-atom incident energy was ~18 meV which

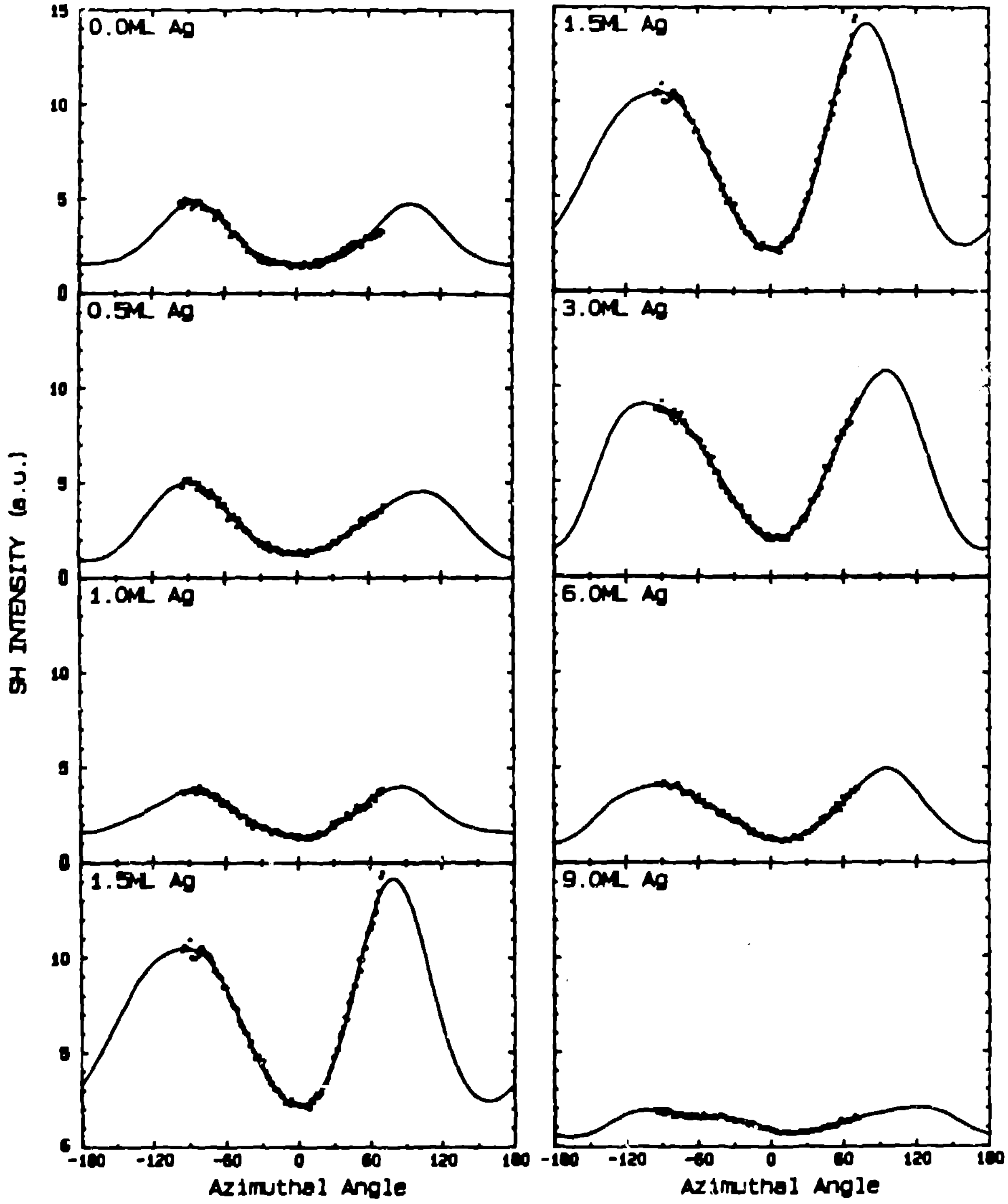

Figure 4. Rotationally azimuthal SH intensity measured at 300 K as a function of Cu(110) surface azimuthal angle at varying Ag surface coverages. The solid lines are theoretical fits to the data discussed in the text.

corresponds to an incident velocity of ~10^5 cm/sec. At such low collision energies the incident He-atom can be expected to interact with the electron density of the Cu surface atoms over a distance of ~5 Å on the incoming and outgoing trajectory. As such the He-atom interaction time with the surface atoms is ~10^{-12} sec. This interaction time is approximately three orders of magnitude longer than that characteristic of x-ray scattering or optical SHG. Assuming that the Cu surface atoms have a vibrational period of ~10^{-13} sec typical of metal surfaces near 300 K, then it can be conjectured that He-atom scattering as an experimental probe measures the time *averaged* structure of the Cu(110) surface. As suggested by the He-atom scattering data, in a time averaged picture the Cu surface atom positions are confined to the [110] rows over the temperature range of <900 K . However, due to a large anharmonicity in the vibrational motion of the Cu surface atoms as a function of temperature, the *instantaneous* positions at elevated temperatures appear disordered. One could then envision a "1-D" type of disorder where the instantaneous Cu surface atom positions in the [110] rows appear to be highly kinked. It is this instantaneous position that is probed by both the x-ray scattering and the rotationally anisotropic SHG experiments reported above.

Over the temperature range of ~900 K a picture of the thermally induced changes in the surface structure that is consistent with all three experimental techniques is one where on the average the surface looks like an ideal corrugated Cu(110) surface but an instantaneous snapshot of the surface would reveal a large amount of 1-D disorder where the rows of Cu atoms are highly kinked. This disorder increases sharply with increasing temperature. Support for this picture comes from the fixed azimuthal angle temperature dependence data reported in Figure 2 at ~75°. The smooth linear decrease with increasing temperature may be due to the increasing 1-D disorder in the rows of Cu atoms. The fact that the data appears to level off above ~700 K might suggest that either the anharmonicity associated with the 1-D disorder cannot increase further or that above this temperature the surface can be viewed as having truly disordered in a 2-D sense.

It is interesting to note that with either s- or p-polarization of the incident radiation a maximum in the SH intensity is observed at azimuthal angles corresponding to increased polarizability across the rows of Cu atoms where the electron density would be expected to be the smallest. A possible explanation of our rotationally anisotropic SHG results involving a subtle distinction between thermally induced electron density delocalization and surface atom displacement also needs to be considered. However, it seems unrealistic that over the temperature range studied the electron density could be uncoupled from the atomic positions.

The rotationally anisotropic SH intensities measured at 300 K as a function of Ag coverage are consistent with the known changes in surface symmetry and structure deduced from LEED and AES studies. The strong enhancement in the SH intensity near 1.5 ML coverage is correlated with the growth of Ag nanoclusters on the surface and is observed at all azimuthal angles. The fact that there are no drastic changes in the anisotropy with increasing Ag coverage confirms that the features observed in the fixed azimuthal angle experiments are not solely determined by changes in the anisotropy but rather by predictable changes in either the surface electronic properties, coverage, morphology, or structure. It is also reassuring that the anisotropy diminishes as the Ag nanoclusters coalesce to form a disordered thick Ag overlayer.

5. CONCLUSIONS

Rotationally anisotropic SHG has been used to study the surface structure and thermal stability of a clean Cu(110) surface and the Ag overlayer structure and Ag 3-D nanocluster growth morphology on Cu(110). The results show clear evidence of the surface structural sensitivity of the optical SHG diagnostic technique. The temperature dependence of the rotational anisotropy from Cu(110) is in agreement with other experiments performed using very different surface probes that indicate a temperature induced change in the Cu(110) surface structure and symmetry above ~600 K.[15,16] We propose that a thermally induce 1-D disordering phenomena accounts for all of the experimental observations.

The Ag coverage dependence of the rotational anisotropy has been shown to be consistent with our previously reported SHG results for the Ag/Cu(110) system and provides important new information regarding changes in the microscopic structure and surface electronic properties that occur with increasing Ag coverage. Experiments currently in progress using a tunable laser source will make it possible to determine the relative contributions of surface interband and free-electron transitions to the SH response. The temperature, coverage, and structural changes in the electronic states giving rise to resonant excitations will also be investigated. Theoretical lattice dynamics calculations should be very useful in understanding the thermally induced vibrational anharmonicity and the microscopic origins of the differences observed in the x-ray, He-atom, and surface SHG experiments. An extension of this work to the Cu(100) and Cu(111) surfaces which have very different thermal behavior and Ag overlayer growth morphologies will be useful in testing the generality of the conclusions drawn from this work. Additional experiments will provide fundamental information important in determining the general utility of optical nonlinear surface spectroscopies as interface specific probes.

6. ACKNOWLEDGMENTS

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