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The growth of Cu layers deposited on Ru(0001) substrates at temperatures between 500 K and 850 K was studied using surface x-ray diffraction. Results are consistent with a Stransky-Krastanov growth mode with a two layer critical thickness.

Introduction

The Cu/Ru(0001) system has been of technological and scientific interest for the last 25 years. This interest is based on the catalytic properties of Ru, which supports hydrocarbon conversion reactions on its surface [1-3]. The activity and selectivity of the reaction can be tuned if group Ib metals like Cu are deposited on the Ru(0001) surface[4,5]. Bimetallic catalysts like Cu/Ru(0001) are heteroepitaxial systems in which the thin epilayer is generally strained due to a lattice misfit. In the case of Cu on Ru(0001), the misfit between the Ru(0001) substrate and the Cu(111) surface is 5.8%. Coherent strain in an ad-layer modifies its electronic band structure and influences both its physical and chemical properties as well as its growth mode [4-6]. Therefore, the study of strain evolution and accommodation in epitaxial systems plays a key role in understanding the behavior of bimetallic catalysts.

Scanning tunneling microscopy(STM) and low energy electron diffraction experiments [7-13] have established that the first Cu layer adopts a pseudomorphic structure in which a hexagonal network of Cu atoms resides in the lateral position, which continues the substrate structure. Due to the lattice misfit between Ru(0001) and Cu(111), this layer is expanded laterally from the ideal Cu-Cu distance resulting in interfacial stress. This stress can be accommodated by the formation of dislocations or by a reconstruction in first or subsequent layers [14]. Not only does stress accommodation play an important role in metal on metal systems, but also in semiconductor devices which are formed by epilayers [15]. In this latter case, it is especially important to understand the strain-induced mechanisms that lead to the degradation of these epilayers and result in a diminution of their performance. In this regard, surfactants play an important role in controlling and improving the layer by layer growth. For metal adsorbate systems, oxygen can act as a surfactant for the growth of Cu on Ru(0001) [16].

When oxygen and other impurities are not present on the Ru(0001) surface, different growth modes for Cu have been observed depending on the experimental conditions. The growth temperature is probably the primary experimental factor, and controls the kinetics on the surface. STM, Auger electron spectroscopy (AES) and thermal desorption spectroscopy (TDS) show that from room temperature up to 540 K, Cu grows in a pronounced island [8,17] or Frank and van der Merve (FM) mode [12]. At higher temperatures, mixed growth modes have been suggested [8, 12]. *In* spite of the large amount of work done on this topic, there are still questions concerning the growth mechanism of Cu on Ru(0001) under near-equilibrium conditions. The uncertainties originate in part from the fact that this system has not been studied systematically in the absence of kinetic limitations and *the* growth mode is strongly influenced by impurities like oxygen and carbon [16].

In this paper, we describe x-ray scattering studies of the behavior of Cu films deposited on clean Ru(0001) surfaces during growth and for temperatures between 500 K and 850 K. Our results suggest that in this elevated temperature range Cu grows in a Stransky-Krastanov growth mode with a two layer critical thickness for coverages up to 6 monolayers (ML) (1ML is defined as the Ru(0001) density, 3.15×10^{15} atoms/cm^2).

Experiment

The x-ray experiments reported in this paper were performed at beamline X22C at the National Synchrotron Light Source (NSLS). Monochromatic x-rays of 10.5 keV are focused to a spot size of 1mm^2 by a cylindrical, nickel coated focusing mirror and a Ge(111) double monochromator. The vertical divergence of the source and the horizontal acceptance of the beamline optics determine the incident beam collimation. In this case, the values are 0.2 and 6 mrad respectively.

Preceding the x-ray experiments, the Ru(0001) crystal, which is 6 mm in diameter and 1.5 mm thick with an orientation accuracy < 0.1°, was mounted into the ultrahigh vacuum chamber of the surface diffractometer [18]. At a base pressure below 1×10^{-10} Torr, the crystal surface was sputtered at 300 K with 1 keV Ar ions. This was followed by repeated cycles of oxygen annealing treatment to remove carbon [19]. At each of these cycles, the Ru crystal was continuously exposed to a partial oxygen pressure of 2×10^{-7} Torr at temperatures between 720 K and 1720 K. It was first heated to 720 K to initiate a surface reaction with the oxygen and subsequently heateded to 1720 K to remove subsurface oxygen and oxygen compounds which formed at lower temperatures [20]. The crystal was then cooled to 720 K, which marks the completion of the cycle. Following the oxygen treatment, the crystal was annealed for 90 min at 2000 K. The sample was heated by electron bombardment from a tungsten filament located between the sample and the sample holder, and the temperature was measured by a W-Re5%-W-Re26% thermocouple. Using an AES system equipped with a cylindrical mirror analyzer, no trace of contamination was found on the crystal surface within the sensitivity of the instrument. Cu was then evaporated onto the Ru(0001) sample from a resistively heated Knudsen cell to produce coverages up to 6 ML. The deposition rate was calibrated using the intensity ratio of the Cu (61 eV) and the Ru (232 eV) AES peaks and from oscillations of the x-ray reflectivity observed close to the anti-Bragg position. The deposition rate was set to 0.1 ML of Cu per minute.

Results and Discussion

Figure 1 shows a model calculation of the (000*l*) rod intensity (x-ray reflectivity) as a function of Q_z for a Ru(0001) surface covered by 0 to 3 ML of Cu. In these models, the assumption is made that the Cu interlayer spacing is the same as in bulk Ru. Small deviations from this ideal spacing by ± 3%, typical of a relaxed surface system, do not change the shape of the calculated reflectivity significantly. Therefore, this model should qualitatively reflect the intensity of the reflectivity during Cu deposition when layer by layer growth is assumed.

The x-ray intensity distribution along the Ru (000*l*) rod represents the Fourier transform of the electron density distribution normal to the crystal surface. Not only can this information be used to determine layer distances, roughness, and thermal parameters at the crystal surface but it can also be used to characterize layer growth during material deposition. For this purpose, it is most useful to study the behavior of the Ru (000*l*) anti-Bragg reflection which is very sensitive to

changes in the electron density caused by material deposition, since the scattering contribution from the crystal bulk is minimal. This follows from Equation 1 on which the above models are based.

$$I(Q_z) = \left| \frac{1}{1 - e^{-iQ_z} e^{\frac{-c_0}{\mu}}} \cdot \sum_b f_b e^{iQ_z z_b} + \sum_s f_s e^{iQ_z z_s} \right|^2 \qquad (1)$$

Q_z corresponds to the momentum transfer of the scattered x-rays normal to the surface and c_0 is the Ru lattice constant normal to the surface. The variable μ represents the x-ray penetration depth. Summations are over bulk (b) and surface (s) atoms in a single unit cell. Within the summations, f_b and f_s are atomic scattering factors of the bulk and surface atoms, respectively, and z_b and z_s are the positional vector components normal to the surface of the respective atomic layer. The first term, which calculates the effect of the break in symmetry at the surface, approaches 0 for $Q_z = 1$. The diffracted intensity is then strongly dependent on the last term of Equation 1, which represents only the diffraction amplitude of the surface structure. It follows that for an even number of deposited Cu layers on the Ru(0001) surface, the intensity reaches a local maximum for $I(Q_z=1)$, whereas for an odd number of layers there is a minimum as can be seen in Figure 1. The integrated intensity of transverse scans at $Q_z = 1$ during Cu deposition should, therefore, oscillate with a period which is equivalent to the deposition of two layers.

Figure 2 shows the experimental results of the anti-Bragg peak intensity behavior for deposition up to 6 ML of Cu on Ru(0001) and for several substrate temperatures. Instead of monitoring the (0,0,0,1) anti-Bragg reflection, we measured the nearby (0,0,0,0.9) reflectivity to avoid possible multiple scattering at the (0,0,0,1) which is not accounted for in equation 1. For temperatures between 500 and 850 K and up to a Cu coverage of 3ML, the growth of three Cu layers on top of the Ru substrate is apparent from the two intensity maxima and minima of the anti-Bragg reflection in Figure 2. After deposition of the third ML, we observed an interesting effect, which was dependent on substrate temperature but independent of coverage.

At a temperature of 720 K, 3 ML of Cu were deposited. Without further deposition, the intensity of the (0,0,0,0.9) reflection increased, which is an indication that the third layer is not stable. The intensity continued to increase until it returned to that observed after completion of the second layer. The same intensity behavior of the (0,0,0,0.9) reflection was obtained at 850 K, after 6 ML of Cu were deposited. For the formation of 6 completed layers, one would expect 3 full oscillations of the anti-Bragg peak intensity, which is not the case. This observation supports the suggestion of a metastable third Cu layer. According to TDS studies, no desorption of Cu is detectable at 850 K [8], which would be an alternative explanation for the above intensity behavior. In order to ascertain whether the growth behavior changes for lower temperatures, the experiment was repeated at a substrate temperature of 500 K with 5 ML of Cu. We observed the same initial intensity behavior of the (0,0,0,0.9) reflection in comparison to that for higher temperatures and Cu coverages up to 3ML. However, for coverages above 3 ML, the final increase of the (0,0,0,0.9) intensity to the value obtained at 2 ML, takes approximately 5 times longer than at higher temperatures.

The above results indicating formation and decay of a metastable third Cu layer raise the question of how the Cu atoms assemble on the Ru(0001) surface. Our results using surface x-ray

diffraction reveal that for Cu coverages above 2 ML, a 2 layer surface reconstruction is formed together with Cu(111) bulk-like islands [22]. New diffraction peaks appear after exposures above 2 ML at a lattice vector appropriate for bulk Cu(111). The intensity of these new peaks continues to grow with exposure.

Conclusions

The growth behavior of thin Cu layers on a Ru(0001) surface was investigated by surface x-ray diffraction as a function of temperature. We have established that after deposition of 6 ML of Cu, only two layers remain stable. We believe the remaining atoms diffuse to form bulk–like Cu(111) islands which cover only a portion of the surface area. It is interesting that a third ML can be formed which is metastable for 500 K $\leq T \leq$ 850 K and that these Cu atoms participate in the formation of Cu islands. At 500 K, diffusion of the Cu atoms seems to be limited since recovery of the anti-Bragg intensity, which indicates the instability of this layer and is a measure for the diffusion rate of Cu atoms, takes approximately 5 to 6 times longer than at $T \geq$ 720 K. At this higher temperature, diffusion of the Cu atoms appears to be much faster than the deposition rate of 0.1 ML per minute. At temperatures where diffusion is not a limiting factor, growth apparently follows a Stranski-Krastanov mode, with a critical film thickness of two layers.

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Figure captions:

Figure 1: Model calculation of the intensity distribution along the (0,0,0,*l*) rod for 0, 1, 2, and 3 ML of Cu on a Ru(0001) substrate.

Figure 2: Integrated intensity of the (0,0,0,0.9) reflection versus Cu coverage for 500 K, 720 K and 850 K.

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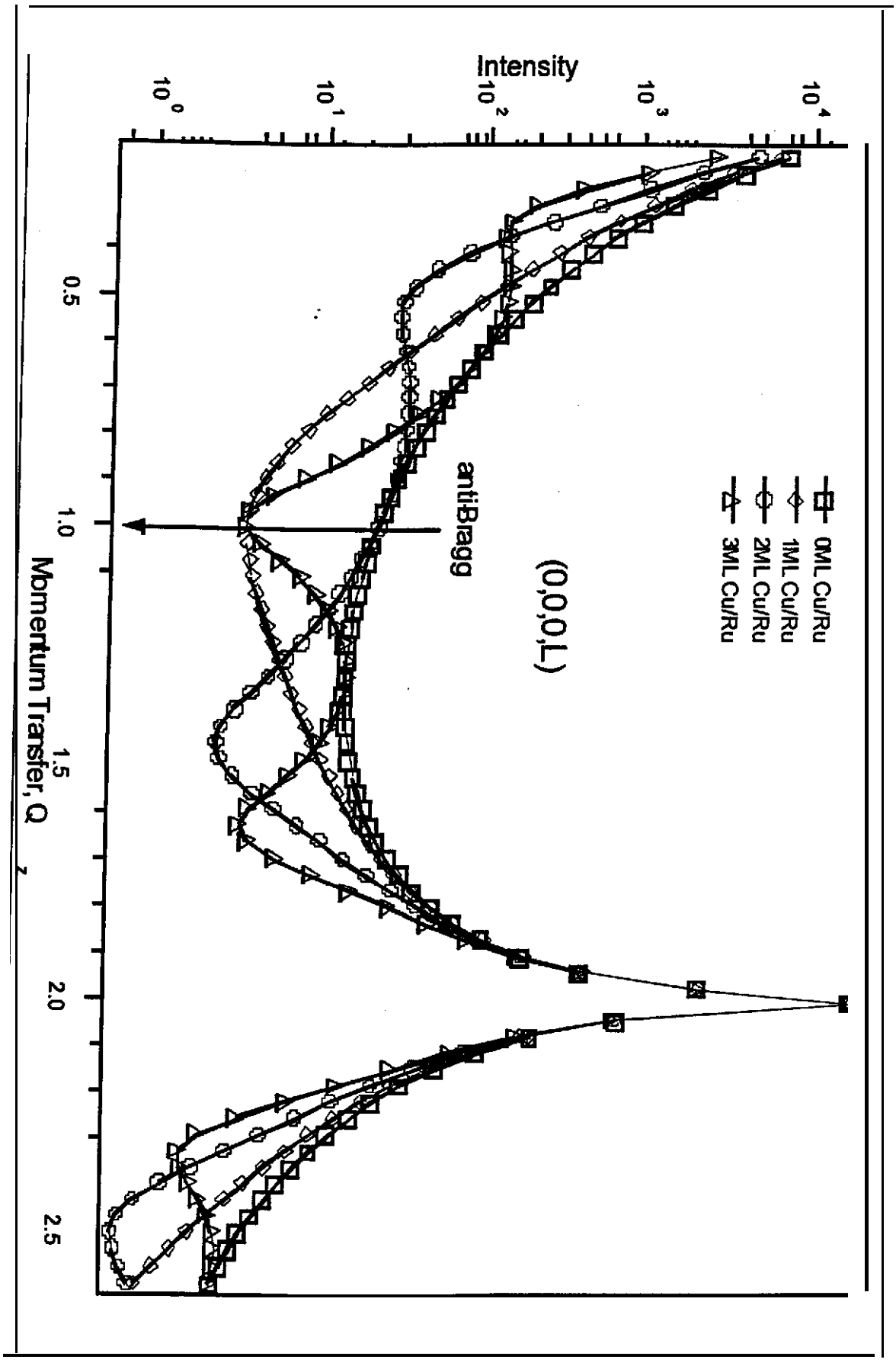
Intensity
10^0
10^1
10^2
10^3
10^4
0.5
1.0
1.5
2.0
2.5
Momentum Transfer, Q_z
antiBragg
(0,0,L)
0ML Cu/Ru
1ML Cu/Ru
2ML Cu/Ru
3ML Cu/Ru

Figure 1

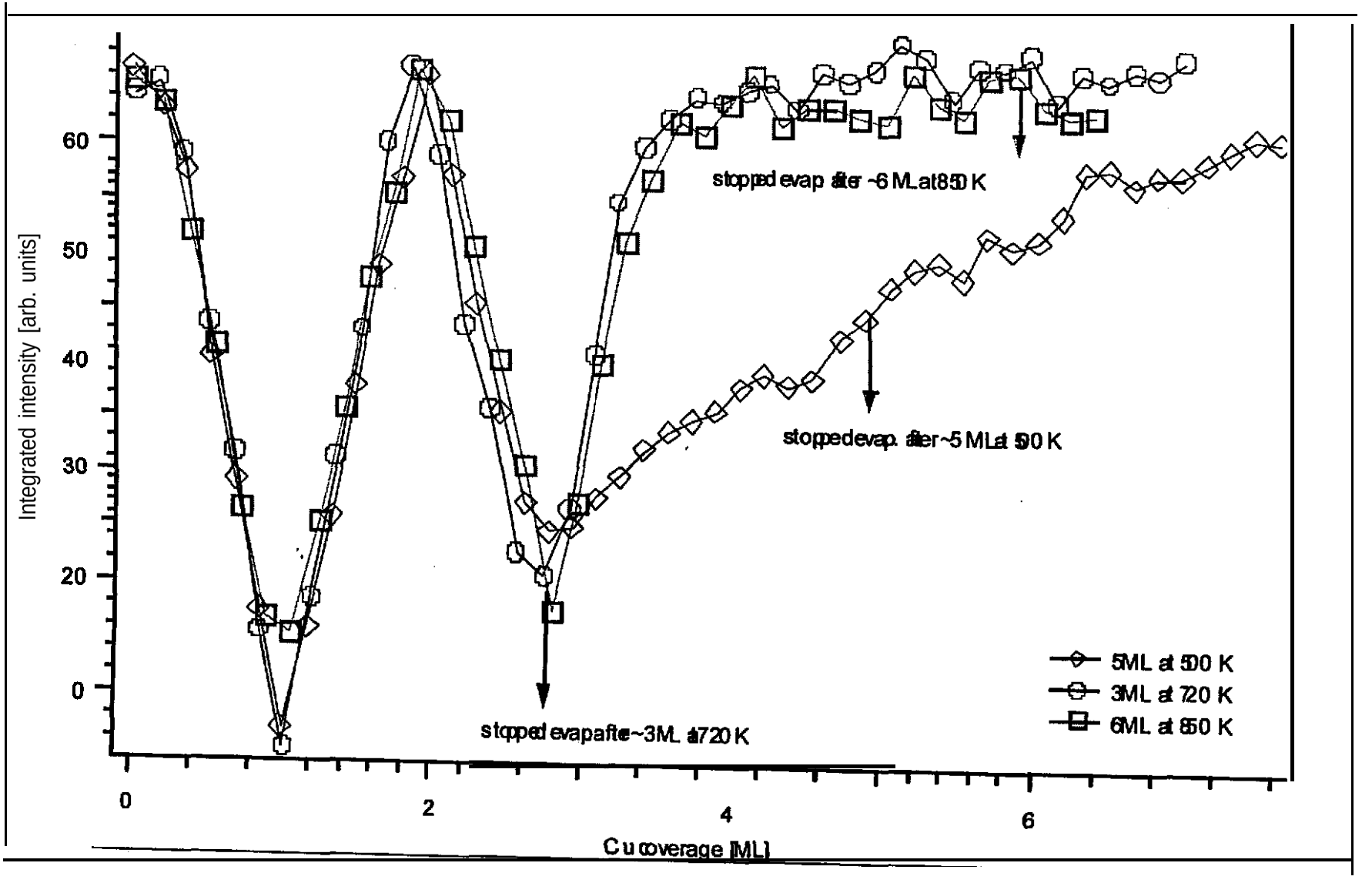
Integrated intensity [arb. units]
Cu coverage [ML]
0
20
30
40
50
60
0
2
4
6
stopped evap after ~6 ML at 850 K
stopped evap. after ~5 ML at 500 K
stopped evap after ~3 ML at 720 K
5ML at 500 K
3ML at 720 K
6ML at 850 K

Figure 2