In-situ reflection high-energy electron diffraction study of epitaxial growth of Cu on NaCl (100) under oblique angle vapor deposition

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ABSTRACT
Epitaxial growth of copper on annealed NaCl(100) surface was carried out using thermal evaporation at an oblique angle of incidence (75 ± 5°) with respect to the substrate normal. The substrate was kept at a temperature of (150 ± 5°C). The crystalline structure of the Cu film was studied in situ by reflection high energy electron diffraction at various deposition times. We observed that the film grows through nucleation of epitaxial islands followed by coalescence and then flattening of the film. The chevron shaped diffraction patterns formed by the refraction effect of electrons were used to identify the crystal facets. With longer deposition times, instead of columnar structures, a continuous epitaxial film was formed despite the oblique angle incidence of the vapor. The morphology of the final film was characterized ex situ by atomic force microscopy and shows L-shaped pores asymmetric with respect to the vapor incident direction.

1. Introduction
Understanding the growth of noble metal such as Cu on an insulator surface is of great interest for various applications such as heterogeneous catalysis, microelectronics, anti-thermic, anticorrosion optical coatings industries, etc., as well as for a fundamental understanding in surface science. It is well known that the substrate temperature, residual vacuum pressure, evaporation rate and contaminants adsorbed on the substrate have an important effect on the structure of the vapor deposited thin film materials [1–3]. A number of studies have been carried out where these parameters are varied during the deposition of various fcc metals on NaCl cleaved on air or vacuum [4–7]. The parallel epitaxy of Cu(001) // NaCl(001) is often observed despite the 36% large lattice mismatch between Cu and NaCl(100). All of these studies were carried out under normal vapor incidence angle.

Over the past several years, modification of the morphology and crystalline structure of thin films by changing the vapor deposition angle has drawn considerable attention [8]. It has been well established that the metal film deposited on amorphous substrates under oblique angle vapor deposition is composed of columnar structures. Moreover, the crystalline orientations on the obliquely deposited films were shown to be different than the normally deposited films [9–11]. The formation of the columnar structure has been attributed to the shadowing effect and random fluctuations during the film growth [12]. Compared with the growth of metals on amorphous substrates by oblique angle vapor deposition, very few studies were done on the oblique angle deposition of metals on the single crystalline substrates [13, 14]. This led us to explore the growth mechanism of Cu on NaCl(100) surface as a generic example of the growth of metal on crystalline substrates under oblique angle vapor deposition.

Reflection high-energy electron diffraction (RHEED) is a well established technique to follow the growth front morphology of epitaxial as well as polycrystalline films [15,16]. Also, to avoid the oxidation and the absorption of contaminants on the film, in situ characterization of the film is highly desirable. The in situ RHEED technique has the ability of monitoring the temporal evolution of the film without exposing the samples to the ambient. In this article we discuss an in situ RHEED study of an epitaxial Cu film grown by oblique angle physical vapor deposition on air-cleaved NaCl(100) substrate held at ~150 °C temperature. The deposition was interrupted at various times for in situ RHEED measurements. The morphology of the final film was also characterized by an atomic force microscope (AFM). We found that despite the obliquely incident vapor, the shadowing effect is suppressed by the epitaxial nucleation and flattening of the top surfaces of nucleated islands. With a longer deposition, instead of columnar structures, a continuous epitaxial Cu (100) film is formed. However, the analysis of electron refraction effect through the crystal showed the presence of asymmetry in the crystalline orientation thus indicating the effect of the oblique angle vapor incidence. Finally an overall picture of epitaxial growth under oblique angle deposition is discussed.

2. Experimental details
2.1. Preparation of NaCl substrate
The NaCl crystal was cleaved along the edge <100> in air. An AFM (Park Scientific Instruments) was used to take the topographic image
of the surface from one of the cleaved pieces, while the other piece was installed on the sample holder with a heating stage in the ultrahigh vacuum (UHV) chamber. Fig. 1 shows the AFM top view image of NaCl(100) surface. The arrangement of the Cu source, the heating stage and the RHEED assembly is shown in Fig. 2(a) and (b). In the AFM image shown in Fig. 1, elongated plateaus with steps along the [010] direction are seen on the surface. The heights of major plateaus are ~1−2 nm, which are several atomic lattice steps/plateau. The overall rms roughness is ~0.6 nm. The surfaces of the plateaus are not flat where smaller steps and defects exist and the rms roughness within the plateaus is ~0.2 nm. The UHV chamber was baked to ~150 °C for ~20 h to degas the chamber wall. The base pressure of the chamber after bake out was approximately 10^{-10} Torr. Moreover, the filament of the deposition source was also degassed prior to the deposition. Also it is well known that the contaminants and the step morphology of the NaCl surface can strongly influence the nucleation and orientation of the first nuclei and the resulting crystal [18–21]. Therefore, the NaCl substrate was annealed from the back side, as shown in Fig. 2(a), at ~450 °C about 3 h in the UHV to remove the adsorbed contaminants and to reduce the twin and the dislocation densities [22]. The RHEED patterns were taken from the NaCl substrate before and after annealing. Fig. 3(a) and (b) show the RHEED patterns taken before annealing along [010] and [110] directions of NaCl(100) surface while Fig. 3(c) and (d) show those after annealing. Before annealing, the diffraction patterns contained spots and did not have strong Kikuchi lines [23] indicating that the surface has atomic scale roughness. This result is consistent with our AFM image (Fig. 1). After annealing, streaked diffraction patterns are clearly seen along the [010] direction and strong Kikuchi lines appear in both directions. This indicates that the annealing efficiently removed any adsorbed layers and reduced defects on the surface making the surface atomically smooth. All the RHEED patterns were taken at a primary electron energy of 9 keV with an incident angle less than 3° (with respect to the substrate surface) and acquired by imaging a phosphor screen using a charge-coupled device (CCD) camera [17] as shown in Fig. 2(b).

2.2. Vapor deposition of Cu on NaCl and in situ RHEED measurements

The copper film was deposited on the annealed NaCl (100) surface using thermal evaporation at an angle of incidence (75±5)° with respect to the surface normal as shown in Fig. 2(a). The NaCl substrate was held at one end with an oxygen free copper clip. The source was made of Cu foil and heated by a W filament. The detailed setup of the deposition source is described elsewhere [17]. The schematics of film growth under shadowing due to oblique angle deposition can be found in reference [11]. During the deposition, the temperature of the substrate was monitored by a thermocouple wire attached to the backside of the substrate as shown in Fig. 2(a) and was maintained at (~150±5) °C. The radiant heat from the Cu source during deposition caused the substrate temperature to rise. To counteract this extra heating, the current to the heater was decreased so as to maintain an approximately constant temperature of the substrate. The epitaxial temperature for Cu growth has been reported to be ~300 °C on air cleaved and around 50 °C on vacuum cleaved NaCl(100) substrate [5]. Even though the NaCl was cleaved in air, it was annealed to remove
contaminants adsorbed. Our choice of substrate temperature is somewhere between these extreme limits to ensure a proper epitaxial growth. The deposition was interrupted at various times viz. 10 min, 40 min (=10 + 30 min), 120 min (=10 + 30 + 80 min), 180 min (=10 + 30 + 80 + 60 min), and 280 min (=10 + 30 + 80 + 60 + 100 min) for in situ RHEED measurements. The duration of each interruption was approximately 15–20 min. After each RHEED measurement the deposition was restarted. The deposition rate was ~1.2 nm/min determined from a Cu film grown under similar growth conditions. After the RHEED imaging of the Cu film deposited for 280 min, the sample was taken out from the chamber and an AFM was used to collect the topographic image of the film. The deposition experiments were repeated twice under similar growth conditions and RHEED images taken at the similar deposition times. In both cases, similar results were obtained.

3. Results and analysis

3.1. RHEED transmission patterns and initial island growth

Fig. 4(a)–(j) show the in situ diffraction patterns taken at various deposition times viz. 10, 40, 120, 180 and 280 min (along the [010] and [110] directions) which correspond to film thicknesses of ~12, 48, 144, 216 and 336 nm, respectively. At 10 min, the diffraction patterns shown in Fig. 4(a) and (b) comprise of spots with a missing specular spot. This is an indication of a rough surface, i.e. island formation. In this case, the RHEED patterns are formed by the transmission of electrons through three dimensional atomic arrangements of these small islands. The lattice constant was found to be (3.8±0.4) Å. This value is consistent with the copper fcc crystal that is 3.61 Å. The deviation in our measured lattice constant from the standard value is basically due to the uncertainty in the measured distance of the phosphor screen from the sample [24]. This result and the symmetry of the diffraction pattern indicate the epitaxy of Cu(001)[100]/NaCl (001)[100], which is one of the orientations for noble metal films deposited on NaCl(100) [3]. With more depositions, the sizes of the diffraction spots shrink as shown in Fig. 4(c) and (d). This implies that while the top surface of the film remains flat, the islands become larger. However, the shapes of diffraction spots show clear irregularities and some of them (indicated by the white arrows) have arc shapes. This indicates that the Cu (001) direction is not exactly along the normal of substrate surface and has certain dispersion (~±5°) around the substrate normal. Moreover, we can also see some weak and uniform ring patterns, which represent the appearance of randomly oriented polycrystalline grains [17]. The lattice constant was also determined from the ring diffraction patterns and was found to be consistent with the (3.8±0.3) Å obtained from the analysis of spot patterns.

3.2. Streaked RHEED pattern and electron refraction

Despite various imperfections in the initial epitaxial growth, for a thicker film (deposition time 120 min or film thickness 144 nm and more), the diffraction patterns basically consist of streaks and clear Kikuchi lines as shown in Fig. 4(e)–(j). As we deposited more, the diffraction patterns from the resulting film became sharper streaks. These indicate the formation of flat top faces of the deposited crystals. Besides these streaks, extra chevrons also appear in the reflection pattern. One of them has been zoomed in as indicated by the white rectangle in Fig. 4(e) and inserted on the top left corner of Fig. 5. The chevron shape originates from the refraction effect [23,25,26] of electron beam when transmitted through the crystals facets. Due to the inner potential of the crystal, the refracted electron beam will be slightly deviated from the incident electron beam depending on the crystal morphology and direction of the incident electron beam. The chevrons due to the refraction effect are identified from the following

Fig. 4. In situ RHEED diffraction patterns from Cu depositions on a NaCl(100) surface in two different directions [100] and [110] taken at times 10, 40, 120, 180 and 280 min which correspond to film thicknesses of (a) and (b) ~12, (c) and (d) ~48, (e) and (f) ~144, (g) and (h) ~216, and (i) and (j) ~336 nm, respectively for a deposition rate of ~1.2 nm/min. The white arrows represent the diffraction spots with partial arc shape. The rectangular frame in Fig. 4(e) is magnified and shown in Fig. 5.
Two signatures. Firstly, the branches of the chevron usually intersect at the point satisfying the 3-D Bragg diffraction condition. Secondly, the chevron extends toward the shadowing edge. In Fig. 4(e), the distance between the point of intersection of the chevron branches and the straight-through electron beam spot was measured to be 3.4 Å⁻¹ which is equal to the length of reciprocal lattice vector of Cu (002).

The effect of electron refraction in the diffraction pattern can be explained following the method of Cowley and Rees [25]. Fig. 5 shows a schematic of the top view of the (001) oriented crystal. When an electron beam is incident along the [010] direction, there are several possible trajectories. For simplicity, consider that the electron beam enters through the facet 1 and exits from the facet 2. The deviation, Δ of the position of the transmitted electron beam from 3-D Bragg diffraction spot is given by,

\[ \Delta = \frac{P}{2E} \left( \frac{n_1}{\cos \phi_1} + \frac{n_2}{\cos \phi_2} \right), \]  

where \( P \) is the inner potential, \( E \) is the primary energy of the electron beam, \( n_1 \) and \( n_2 \) are the vectors normal to the facets 1 and 2, \( \phi_1 \) and \( \phi_2 \) are the angles between the electron beam and the facet normals respectively. This trajectory will contribute to the left branch (branch A in Fig. 5) of the chevron, which has an angle \( A \) of approximately 29° with respect to the central vertical line. If we assume that the edges of the top facet are along the fast diffusion direction, i.e. along [110]–, then the facet 1 is \((\overline{1}13,n)\) plane and the facet 2 will be \((1,1,n)\). Due to the symmetry of the crystal with respect to the incident vapor flux direction \( \phi_1 \) is equal to \( \phi_2 \). Considering Eq. (1) and only the deviation in the direction, we can write

\[ \cos(A) = \frac{n}{\sqrt{l^2 + n^2}}. \]  

We can see that for the first several low index crystalline planes, such as \((111), (112), (113)\), the corresponding \( A \) will be 45°, 26.6° and 18.4°. The experimental value of ~29° is closer to 26.6°, therefore the facets 1 and 2 facing the flux are mainly the (112) planes. The electron beam that goes through the facets 4 and 3 will contribute to the right branch of the chevron (branch B in Fig. 5). The angle \( B \) for the right branch of the chevron has a similar value of ~30°. Other trajectories, which enter the facet 5 and exit from the facet 2 or 3, will basically cause the electron beam to move straight down towards the shadowing edge. Similar analyses were done with chevrons of diffraction patterns shown in Fig. 4(g)–(j). With longer deposition time, the film becomes thicker as well as more continuous and the electron refraction is smeared. The angles \( A \) and \( B \) are slightly larger in the [010] diffraction pattern from 216 nm thick film (Fig. 4(g)), which are approximately 30° and 32° respectively, whereas chevrons are barely detectable in Fig. 4(i) or Fig. 4(j). The (112) planes have an angle of 35.3° with respect to the substrate normal [001]. These facets are steeper, i.e. have larger angles with respect to (100) planes compared to the facets (113), (115) and (117) usually formed under normal vapor depositions. The observation of the higher slope of the side facets could be due to obliquely incident vapor, in which the atoms will asymmetrically land on the islands. Specifically, both the shadowing effect and steering effect are argued to contribute to the steeper slopes of the side facets. Under steering effect the atoms experience extra attraction of van der Waals force from the protrusions such as islands [27,28].

### 3.3. Ex situ AFM image of Cu film

After the total deposition time of 280 min (336 nm film thickness) the sample was taken out of the chamber for AFM imaging. Fig. 6(a) shows a (1 µm × 1 µm) topographic image of the surface of the Cu film. This image shows that the final film is very flat with some asymmetric L-shaped pores with respect to the vapor incident direction. The edges...
of the pores are mostly along the [110] direction consistent with a low diffusion barrier along close packed step edges [29]. The flat surface of the Cu film is consistent with the previously obtained streaky diffraction patterns.

To obtain information on the orientations of the crystal facets, several lines were drawn across the L-shaped pores in the AFM image and the height profiles were analyzed. One such profile is depicted in Fig. 6(b). The angles $\alpha$ and $\beta$ were obtained by the linear fit of the slanted portions of the height profile as shown in the Fig. 6(b) and were found to be $(42 \pm 4)^\circ$ and $(48 \pm 6)^\circ$, respectively. Both values are larger than 35.3°, the angle formed between the (112) and (001) of an fcc structure. The discrepancy between the observed and the expected values can be attributed to the complicated tip convolution effect on the AFM image and an error due to small sampling. The high surface energy might also drive the facets to form (111) planes for minimizing the energy.

4. Discussion

4.1. Initial island growth

The structure and orientation of a metal deposited on an insulator surface depend on various parameters of which the most important ones are deposition rate, substrate temperature, presence of defects or contaminants adsorbed on the substrate surface, step pattern of the substrate and nature of the bonding between the metal atoms and the insulator surface. A theoretical study of the adsorption of Cu atom on the NaCl(100) surface through an embedded cluster approach by Mejias [31] found that the Cu atoms have a preferential adsorption on the cationic positions with an interaction energy of ~0.1 eV. This interaction is mainly electrostatic in nature and does not have an appreciable contribution from chemical interaction between Cu and ionic surface. This implies that the metal grows in the Volmer–Weber (3-D) island mode. This is implied by the spots observed in the diffraction patterns of Fig. 4(a) and (b). The orientations of the nuclei can be inferred to be the [001] from these diffraction patterns. One might also expect that the initial nucleated grains have the [111] orientation which minimizes the surface energy. Actually in Fig. 4(a), the weak diffraction spot pattern does show the existence of a small amount of second generation twin structure of the (111) plane on the surface. However, the major diffraction spots represent the epitaxial grains with the [001] orientation. The incident vapor flux on the atomic steps present on the substrate leads to a decoration pattern with occasional anomalous orientation of the initial nuclei as suggested in references [19,21]. With a deposition rate of ~1.2 nm/ min and a substrate temperature of ~150 °C, our observation of the initial nuclei orientation is consistent with the results in the literature [1,3,5].

Tanaka et al. [32] have found that the quality of an epitaxial film is greatly enhanced by increasing the defects on NaCl(100) substrate using electron bombardment. Through the classical model of interatomic interactions Venables and Harding [33] have shown that the binding energy between noble metal atoms and the defects on NaCl substrate could be as large as ~0.6 eV due to the much greater electrical field gradient around those defects. Therefore, we expect that most copper atoms initially condense around the defects and spread out resulting in an epitaxial film. This is consistent with the observed slightly out-of-plane orientation of the epitaxy shown in Fig. 4(b), which can be argued to be the result of conformal growth on the defects of the substrate. The mechanism of initial alignment of the epitaxy is still not exactly known, however the large lattice mismatch of 36% ($\left(\frac{\alpha_{\text{NaCl}} - \alpha_{\text{Cu}}}{\alpha_{\text{NaCl}}}\right) = \left(\frac{5.65 - 3.61}{5.65}\right) \text{ Å/Å ~36\%}$) can be accommodated by a 2.5% biaxial stretch in [100] and [010] directions, which gives a NaCl-Cu lattice matching of 2:3 to form a commensurate epitaxial growth [34]. This 2:3 lattice match is supported by the reciprocal rods spaced observed in Fig. 3 for clean NaCl and in Fig. 4 for Cu covered NaCl.

As the Cu film thickness increased, the corresponding RHEED patterns showed both spots and additional weak rings (see Fig. 4(c) and (d)). The ring intensity seems to be uniform implying no preferred texture formation. The appearance of polycrystalline grains is very sensitive to the deposition conditions. Among many sources, contamination induces some random orientation on the film and most likely affects the regions where the grains merge. In a similar setup of experiment with short deposition and lower substrate temperature, we found that the film could be dominated by polycrystalline grains, where the corresponding AFM images, not shown here, consist of small and random islands instead of flat surface. It is important to note that the overall deposition was carried out in five steps with interruption periods of 15–20 min each for taking RHEED images. During the period of interruption, the base pressure in the chamber was ~5 × 10⁻¹¹ Torr, so the possibility of contamination to the growing crystal is low. Therefore we assume that the growth of the crystal is continued from its previous stage and not by repeated nucleation. Moreover, in a study of Cu texture evolution under interrupted growth conditions, Tang et al. [11] did not observe any noticeable signature of interruption in the morphology and the texture of the growing nanorods, provided that a good vacuum condition and a stable temperature are maintained.

4.2. Formation of a continuous film at later stage of growth

Upon further Cu depositions the spots and rings in the RHEED patterns disappeared and vertical streaks formed and became sharper. This implies the grain growth and island coalescence. During these processes, the top surfaces remain flat implied by the streaked diffraction patterns, which indicates the high diffusion of surface atoms. The flat top geometry also significantly reduces the effect of oblique angle vapor incidence, in which the side facets of the islands are not efficiently shadowed by its neighboring grains. This is consistent with our ex situ AFM image shown in Fig. 6(a). In this image, a basically continuous film with some L-shaped pores is found. The presence of L-shaped pores is a signature of the oblique angle deposition and is primarily due to the fact that shadowing tends to inhibit the coalescence of islands along the direction parallel to the beam while in the direction perpendicular to the beam there is no such restriction. The present experimental result is in contrast with the square-shaped homoepitaxy mounds observed under normal vapor deposition of Cu [35]. Shim and Amar [14] have studied the effect of geometrical shadowing on the evolution of the morphology of epitaxial film grown at room temperature or below. In their work, a simplified model of fcc (100) homoepitaxial growth was used in which the effects of shadowing are included but not the additional modifying effects such as short and long range attraction. They have shown that most of the features observed in Cu (100) growth including the existence of a transition from anisotropic mounds to ripple formation and finally to rod formation (with higher oblique incident angle), could be primarily explained by the geometrical effects. In particular, for a slow deposition rate at an oblique angle of ~70°, shadowing effect has been argued to lead to a preference for mounds to coalesce along the direction perpendicular to the incident vapor beam and onset of ripple formation. The present experiment was conducted at an oblique incident angle of ~75° and at a substrate temperature of 150 °C. While the deposition angle used in our experiment is similar, the deposition temperature is relatively higher than those used in the simulation of reference 14. We observed that the degree of mounds coalescence in the direction parallel to the vapor flux is less than that in the perpendicular direction as indicated by the L-shaped pores. It is well known that the temperature plays a critical role [5] in the epitaxial growth of the films. The present experimental observation of basically a flat film with no ripple formation indicates that the mounds coalesce...
in both perpendicular and parallel to the vapor beam direction owing to a high surface diffusion of the Cu atoms at the substrate temperature used during our experiment.

5. Summary

Using in situ RHEED and ex situ AFM we monitored the growth of Cu on air-cleaved NaCl (100) under oblique angle vapor incidence. Despite oblique vapor incidence, the initial Cu growth was observed to be dominated by parallel epitaxial islands with orientation Cu (001)[100]//NaCl (001)[100] as in normal vapor deposition. The spot diffraction patterns for shorter deposition times, spots accompanied by rings for moderate deposition times followed by sharp streaks for longer deposition times represent the sequence of growth events as nucleation of epitaxial islands followed by coalescence and then the formation of flat film. The presence of grains composed of second generation twins of (111) planes are argued to induce random oriented grains in the moderate deposition times. With a longer deposition time, instead of columnar structure, a continuous epitaxial film was observed to form with asymmetric L-shaped pores that have edges along the <110> directions. These L-shaped pores were attributed to the asymmetric supply of mass during the oblique angle deposition. In addition to the investigation on the orientations of the top faces of crystals, we also found that the side facets of the crystal are dominated by (112) planes as observed by analyzing the refraction effect of the electron beam.

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