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Copper Nanoclusters Electrochemically Deposited on *p*-GaAs(100) in H_2SO_4 Solution Probed by Surface-Sensitive XAFS

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Abstract

The local structure of electrochemically deposited Cu on *p*-GaAs(100) has been investigated by *in-situ* surface-sensitive X-ray absorption fine structure (XAFS). The Cu overlayers were deposited on *p*-GaAs(100) (dopant density : 1.0×10^{19} cm^{-3}) in an electrochemical cell filled with 0.1 M H_2SO_4+0.1 mM $CuSO_4$ solution. The Fourier transform (FT) of the Cu K-extended X-ray absorption fine structure (EXAFS) oscillations for the Cu overlayers on GaAs with the electrical field vector ε parallel to the surface indicated that the Cu nanoclusters with a fcc-like short range order are formed as the deposition proceeds above a critical coverage $\theta_c \sim 0.25$ ML. The second and third nearest neighbor peaks in the FT increase in intensity for $\theta > 1$ ML. This indicates the three-dimensional growth begins in an early stage ruling out a Stranski-Krastanov (SK) mode growth. We find that the FT results for the initial deposition ($\theta < 1$ ML) show a remarkable difference in the short range order. Two nearest neighbor peaks observed at 1.9 Å and 2.1 Å indicate that Cu atoms strongly interact with oxygen atoms and suggest that small Cu clusters such as dimers are formed in the early stage of deposition.

1. Introduction

Electrochemical deposition of metal overlayers onto semiconductor surfaces attracts much attention as a promising means to form nanoclusters without using ultra high vacuum (UHV) environments. In order to achieve atomically controlled nanoclusters or metal-semiconductor interfaces, it is essential to establish the growth mechanism from microscopic viewpoints. The scanning probe microscopy techniques such as tunneling microscopy (STM) and atomic force microscopy (AFM) are now recognized as powerful tools for the *in-situ* examination of the surface topography of an electrode with a spatial resolution up to atomic level [1]. For electrochemical deposition of metals onto semiconductor surfaces, AFM has been successfully used [2]. These techniques, however, can provide only the geometrical arrangement of surface atoms and the information on the site-selective local structure, chemical bonding and the average structure of overlayer is missing.

Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) are useful techniques to obtain the information on the local structure around a particular species of atom on the electrode surface even in solution. However, for applications of EXAFS/XANES to *in-situ* studies for electrochemical deposition, high surface sensitivity is required to investigate the overlayer structure over a wide range in film thickness. For a normal incidence geometry in a hard X-ray region, the probing depth is much greater than a typical layer thickness in surface studies (~3 Å). Below a critical angle, however, X-rays are totally refracted as they cross the interface between the two media reducing the probing depth by several orders of magnitude. Using a grazing-incidence geometry and an energy discrimination of fluorescence spectra, sub-monolayer surface sensitivity has been achieved [3]. Here we report the *in-situ* EXAFS and XANES studies of the electrochemical deposition of Cu nanoclusters on *p*-GaAs(100) in H_2SO_4 solution.

2. Experimental

Single crystalline Zn-doped *p*-GaAs(100) wafers (Mitsubishi Chemical Corp., doping density $1.0\times10^{19}cm^{-3}$) were used as samples. Prior to experiments, samples were cleaned in hot acetone and ethanol and rinsed with Milli-Q water (Millipore Co.). Ohmic contact was secured using an In-Zn alloy. The details of electrochemical deposition are reported elsewhere [4]. A multipole wiggler (MPW) magnet inserted in a straight section of the 2.5

GeV storage ring (BL13B) at the Photon Factory was used as a light source. With the maximum magnetic field B_0 (1.5 T) a high flux greater than that of a bending magnet by an order of magnitude is obtained extending over a wide energy (4-30 keV). Using a directly water-cooled crystal, the energy resolution $\Delta E/E$ ~2×10^{-4} was obtained which is sufficient for B_0 below 1.25 T. A pure Ge detector array with 19-elements [5] was used to measure the fluorescence yield of Cu K_α in a grazing incidence-excitation mode. The grazing angle of the incident beam was set at 0.4-1.6 degree. The GaAs samples fixed on the sample holder made by PCTFE by using epoxy based adhesive (Chiba-Geigy, Araldite) was set to an *in-situ* electrochemical cell (PCTFE). A 6.0 μm thick Mylar film (Chemplex) was used as a window. The measurement was carried out in 0.1 M H_2SO_4+0.1 mM $CuSO_4$ solution. The applied potential was referenced to an Ag/AgCl electrode connected to the cell through a capillary tube and was controlled by potentiostat (Nikko Keisoku, SPOT2501). When the negative potential is applied to GaAs electrode, the electrolyte solution is injected to the electrochemical cell and the thickness of the solution onto the electrode is kept with more than 1 mm. During the EXAFS/XANES measurements, most of the $CuSO_4$ solution was removed from the cell by pumping.

3. Results and Discussion

Figure 1 shows the fluorescence yield spectrum for copper overlayers (1 ML) deposited on *p*-GaAs(100) taken with the electrical field vector ε parallel with the surface. Above the K-shell absorption edge (8.98 keV), the fluorescence yield reflects the modulations in absorption cross section due to the interference of photoelectrons emitted by the excited atoms over a wide energy range. The normalized EXAFS oscillations of Cu overlayers on GaAs(100) are plotted in Fig. 2, as a function of photoelectron wavenumber k (Å^{-1}) for various surface coverage θ (5×10^{-2} to 6 monolayers (ML's)). On increasing θ, the envelope of EXAFS systematically changes indicating the coordination of excited copper atoms increases and for θ > 1 ML, the dominant scattering atoms are Cu atoms which form a fcc structure. Utilizing the profile of EXAFS envelopes, the atomic species around Cu atoms can be analyzed. The dominant scatterer atoms were identified as Cu for θ > 1 ML. The *k*-

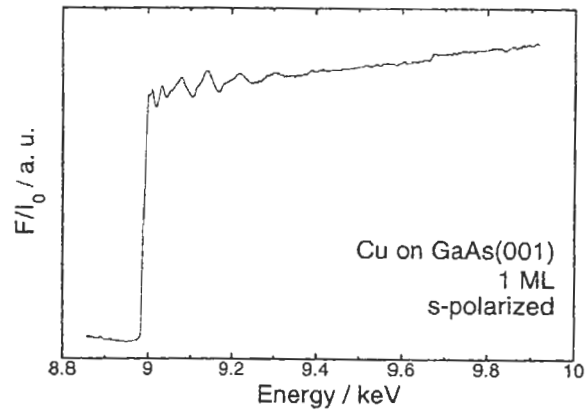

Fig. 1 Cu K-fluorescence yield spectrum for copper overlayer (1 ML) electrochemically deposited on *p*-GaAs(100) taken with the electrical field vector ε parallel to the surface.

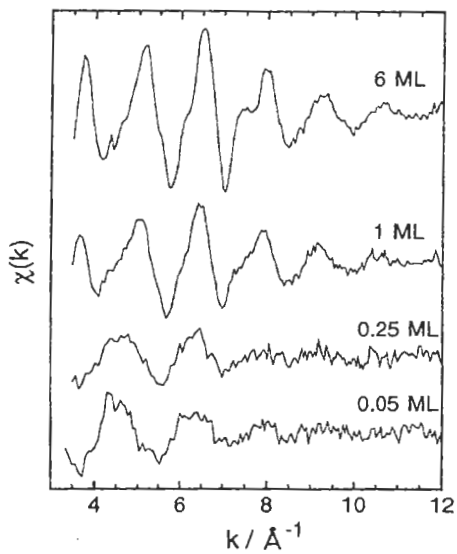

Fig. 2 Cu K-EXAFS oscillations for copper overlayers on *p*-GaAs(100) with various coverage.

dependencies of the total phase shift and backscattering amplitude functions for Cu and light-element atoms such as oxygen are quite different: $|f_o(\pi,k)|$ peaks at low k and falls off sharply with the increase of k while $|f_{Cu}(\pi,k)|$ has a maximum at k = 6-7 Å^{-1} and extends to a region with k > 15 Å^{-1}.

In Fig. 3, the magnitude of Fourier transform (FT) for the Cu K-EXAFS oscillations of Cu overlayers on GaAs(100) is shown for the same data set shown in Fig. 2. The FT results show a systematic change of the radial distribution which indicates that the Cu nanoclusters with a fcc-like short range order are formed as the deposition proceeds above a critical coverage θ_c ~ 0.25 ML. As θ increases further, the Cu coordination number and the Cu-Cu distance increase approaching the fcc values. For θ > 1

ML, the magnitude of second and third nearest neighbor peaks in the FT increases in intensity as the average cluster size increases. Interestingly, the fcc-like short range order appears before 1 ML Cu overlayer is deposited. This suggests that the three-dimensional growth begins in an early stage, consistent with AFM observation [2]. Thus the growth mode is not described by a Stranski-Krastanov (SK) mode where the initial layer-by-layer growth turns into a three-dimensional one above a critical thickness. The development of a fcc-like short range order is also observed in the XANES spectra as illustrated in Fig. 4. From a systematic variation of XANES, it is also concluded that the characteristic features of a fcc structure develops for $\theta > 1$ ML.

On the contrary, the FT results for the initial deposition ($\theta < 1$ ML) showed a remarkable difference in the short range order. From Fig. 3, it is clear that there are two peaks separated by 0.5 Å which are both shorter than the Cu-Cu distance in fcc Cu metal. The nearest neighbor peak consists of the short bond A (1.9 Å) and the longer bond B (2.12 Å). From the *k*-dependence of EXAFS profile, the former is ascribed to the Cu-O bond while the latter is due to either Cu or substrate atoms (Ga or As). The short bond A is easily ascribed to the oxygen atoms. For the longer bond B, one can not distinguish the atomic species. However, since the polarization is parallel with the surface, peak B is likely to be the Cu-Cu correlation. The detailed discussion on the origin of the two peaks will appear elsewhere. Here, we note that the bond length B coincides with the Cu-Cu distance reported for Cu dimers [6]. The results may indicate that the Cu dimers are formed prior to the growth of nanoclusters stabilized by oxygen atoms of solution.

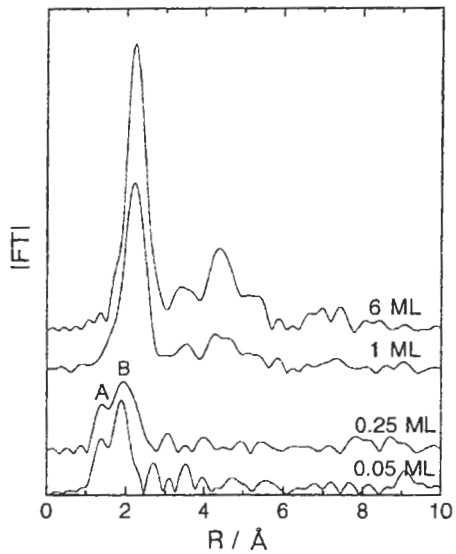

Fig. 3 Magnitude of Fourier transform for the EXAFS data shown in Fig. 2.

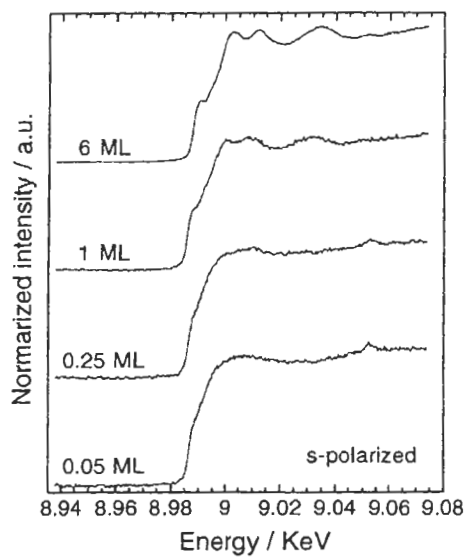

Fig. 4 Cu K-XANES spectra for copper overlayers electrochemically deposited on *p*-GaAs(100) with various coverage.

4. Conclusion

The local structure of copper nanoclusters electrochemically deposited on *p*-GaAs(100) was studied by *in-situ* surface-sensitive XAFS. The Cu K-EXAFS shows that on increasing the coverage beyond a critical value (1 ML), copper nanoclusters with a fcc-like short range order is deposited. Since the island growth is observed prior to the nominal coverage of 1 ML, the growth mode is not a Stranski-Krastanov type, in agreement with the previous AFM observation. However, in the low coverage region, we observed that the local structure of deposited copper atoms features remarkably different short range order. Two distinct peaks were found in the FT around excited copper atoms, which are likely to be due to the oxygen atoms and Cu or Ga/As atoms. Since the latter peak is polarized strongly parallel to the (100) surface and the distance is close to the reported value for Cu dimers, it is likely that the copper atoms form dimers oriented parallel to the surface, in the initial stage of deposition. This state is in sharp contrast to the island growth regime.

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