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In Situ Optical and Electrochemical AFM Monitoring of Cu Electrodeposition Process on Bare and \( \text{NH}_4 \text{S}_2 \) Treated p–GaAs(001) Surfaces

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The initial process of Cu electrodeposition on bare and (NH₄)₂S-treated p-GaAs(001) surfaces was investigated using electrochemical, reflectance, light-scattering, and in situ electrochemical atomic force microscopy (AFM) measurements. The reflectance and light-scattering measurements showed that on both the bare and (NH₄)₂S-treated surfaces, Cu deposition occurred in a cluster growth mode and the Cu clusters grew in the z-direction at a relatively negative potential where the limiting current was observed. The potential dependencies of the reflectance and scattered light intensity obtained at various potential scan rates showed that the size of the Cu clusters was smaller at the higher scan rate. The charge due to the Cu deposition at the (NH₄)₂S-treated electrode was nearly half that of the bare surface under the same experimental conditions, and AFM images showed a smaller number of Cu clusters at the (NH₄)₂S-treated surfaces, suggesting a reduction in the defect sites by the (NH₄)₂S treatment.

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where \( R(E) \) and \( R_0 \) are the reflectivities at a given potential, \( E \), and at the potential where no deposition takes place, respectively.\(^{23}\)

*In situ* electrochemical AFM measurements were carried out using a Nanoscope II or E controller with an electrochemical AFM unit (Digital Instruments) in a constant force mode. The spring constant of the cantilevers was 0.58 nN/m. A glass fluid cell supplied by Digital Instruments was used. A Pt wire and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. Details of the AFM measurements were previously described.\(^{23}\)

**Results and Discussion**

**Deposition on a bare GaAs surface.**—Figures 1-4 show the simultaneously obtained potential dependencies of current, \( \Delta R/R \), and scattered light intensity change at the p-GaAs(001) electrode measured in 0.1 M \( \text{H}_2\text{SO}_4 \) solution containing 1 mM CuSO\(_4\) when the potential was scanned between \( +0.1 \) and \( -0.49 \text{ V} \) at various sweep rates. The scattered light intensity was reported with respect to that at \( +0.1 \text{ V} \).

When the potential was scanned from \( +0.1 \text{ V} \) in the negative direction at a scan rate of 2 mV s\(^{-1}\) (Fig. 1), the cathodic current started to flow at ca. 0 V, reached a maximum at \( -0.14 \text{ V} \), and decreased to a relatively constant value. The \( \Delta R/R \) increased very slightly and the scattered light intensity did not change at the beginning, but when the current approached a peak at \( -0.14 \text{ V} \), the \( \Delta R/R \) and the scattered light intensity started to decrease and increase sharply, respectively. At ca. \(-0.24 \text{ V} \) where current reached a constant value, the \( \Delta R/R \) value started to increase and the increment of the scattered light intensity became less significant. Even after the potential scan was reversed to the positive direction at \(-0.49 \text{ V} \), a cathodic current still flowed and both the \( \Delta R/R \) and the scattered light intensity increased at a constant rate. At ca. \(-0.12 \text{ V} \) where the cathodic current still flowed, the \( \Delta R/R \) became constant and the scattered light intensity started to increase. The current became anodic at ca. \(-0.09 \text{ V} \). As the potential became more positive, the \( \Delta R/R \) value in the negative potential scan and the maximum of the scattered light intensity stayed at its original value as the potential was scanned more positively.

Although similar potential dependencies of current, the \( \Delta R/R \) value, and the scattered light intensity were observed at all the scan rates (Fig. 2-4), several scan rate–dependent features were noticed. Potentials for the cathodic and anodic current peaks shifted toward the negative and positive directions, respectively, and the minimum of the \( \Delta R/R \) value in the negative potential scan and the maximum of the scattered light intensity became smaller as the scan rate increased. When the scan rate was 2, 5, 10, and 20 mV s\(^{-1}\), the minimum of the \( \Delta R/R \) value was \(-13, -10, -4, \) and 0%, and the maximum of the scattered light intensity was 500, 250, 60, and 10, respectively. Furthermore, the minimum and the maximum of the \( \Delta R/R \) value observed in the positive potential scan became less significant as the scan rate increased.

To analyze these results in more detail, the \( \Delta R/R \) value and the scattered light intensities obtained at the various sweep rates were plotted as a function of the charge passed during the deposition in Fig. 5. The charge dependencies of the \( \Delta R/R \) value and the scattered light intensity showed a minimum, increased again, and reached a maximum when current reached the maximum. The scattered light intensity decreased to its original value at the potential where the current reached a maximum. After the current reached a maximum, the \( \Delta R/R \) value decreased to its original value and the scattered light intensity stayed at its original value as the potential was scanned more positively.
light intensity clearly showed that the deposition process can be divided into three regions. In the first region, the $\Delta R/R$ value increased very slightly and the scattered intensity did not change despite the current flow. There is no obvious relation between the sweep rate and the charge passed in the first region. In the second region, the $\Delta R/R$ value decreased in proportion to the charge with almost the same rate at all scan rates except in the case of 20 mV s$^{-1}$. The scattered light intensity increased in proportion to the charge in this region. The slope depended on the scan rate in this case with the smaller values at the higher scan rates. In the third region, the $\Delta R/R$ value linearly increased with the charge with a constant rate at all scan rates. The scattered light intensity also increased linearly with the charge but at a much smaller rate than in the second region.

For the three-phase system such as the present case, i.e., (i) the bulk electrolyte, (ii) the thin film, and (iii) the bulk electrode, when the thickness of the thin film, $d$, is much smaller than the wavelength of the incident light, $\lambda$, $\Delta R/R$ is given by:

$$\frac{\Delta R}{R} = \frac{8\pi d\epsilon_1 \cos \varphi}{\lambda} \text{Im} \left( \frac{\epsilon_2 - \epsilon_3}{\epsilon_1 - \epsilon_3} \right)$$  \[2\]

where $\varphi$ is the incident angle, $\epsilon_1$ is the dielectric constants of the electrolyte, and $\epsilon_2$ and $\epsilon_3$ are the complex dielectric constants of the film and the substrate, respectively. $\epsilon$ is given by

$$\epsilon = \epsilon' - i\epsilon''$$  \[3\]

where $\epsilon'$ and $\epsilon''$ describe the dispersion and absorption in a medium, respectively. Equation 2 shows that the $\Delta R/R$ value is proportional to the thickness of the thin film as long as the complex dielectric constants of the thin film are independent of the thickness.
According to the Rayleigh scattering theory, when the size of the cluster is much smaller than λ, the scattered light intensity, \( I \), is given by

\[
I = \frac{\pi^2}{2} \frac{1}{\lambda^4} \frac{N^2}{\varepsilon_0^2} \cos^2 \theta \loyd^2 I_0 \tag{4}
\]

where \( \theta \) is the scattering angle, \( N \) is the number of the scatterers, \( V \) is the volume of the scatterers, \( \varepsilon_0 \) is the permittivity of the free space, \( r \) is the distance between the scatterers and the detector, and \( c \) is a constant. This relation shows that the scattered light intensity is proportional to the square of the volume of the cluster and the number of clusters.\(^{11,24}\)

Vereecken et al. have reported that the reduction of \( \text{Cu}^{2+} \) to \( \text{Cu}^0 \) proceeds by a one-step reaction in a solution containing sulfate anion.\(^1\) Thus, the cathodic current observed in this study should be mainly due to the electrodeposition of \( \text{Cu} \), and a simulation of the \( \Delta R/R \) for the electrolyte/Cu/GaAs three-phase system based on Eq. 2 showed that the \( \Delta R/R \) value increases with the thickness of \( \text{Cu} \).\(^{23}\) In the first region, however, the \( \Delta R/R \) value increased very slightly and the scattered light intensity did not change even though a cathodic current flowed. One possible reason for this observation is an electrochemical cathodic reaction other than the \( \text{Cu} \) deposition, e.g., the electrochemical reduction of surface oxides on GaAs such as \( \text{As}_2\text{O}_3 \), \( \text{As}_2\text{O}_5 \), and/or \( \text{Ga}_2\text{O}_3 \)\(^{19,25}\) took place. A simulation of the \( \Delta R/R \) value for electrolyte/GaAs oxide/GaAs three-phase system based on Eq. 2 with the complex dielectric constants of the surface oxide\(^{25}\) showed that the \( \Delta R/R \) value increases if the surface oxide is removed. In the present result, the \( \Delta R/R \) value increased very slightly at the beginning, and the thickness of the oxide layer estimated by the charge passed as well as the increase in the \( \Delta R/R \) value in the first region was \( \text{ca.} \) 1 nm, which is in agreement with the value of 1-3 nm as the thickness of the native surface oxide previously reported.\(^{19,26}\) The variation in the charge passed in the first region should be due to the difference in the thickness of the surface oxide, which depended on the experimental procedure. Thus, we can conclude that the electrochemical reduction of GaAs oxide occurred in the first region.

After the electrochemical reduction of the surface oxide was completed, the electrodeposition of \( \text{Cu} \) started and the cathodic current sharply increased (second region). In this region, the scattered light intensity increased, and the \( \Delta R/R \) value decreased as the electrodeposition of \( \text{Cu} \) proceeded. The decrease in the \( \Delta R/R \) value should be caused by the increase in the scattered light, which reflects the increase in the surface roughness. Thus, \( \text{Cu} \) clusters grew mainly in size not in number with the increase in the amount of electrodeposited \( \text{Cu} \). These results support our previous results that \( \text{Cu} \) clusters grew in size by an instantaneous nucleation process during the initial stage.\(^4\) The higher the sweep rate, the lower the maximum of the scattered light intensity as shown in Fig. 5. Equation 3 shows that a smaller cluster and fewer clusters, i.e., a smoother surface, gives a less scattered light intensity. Thus, this scan rate dependence of the change of the intensity in the scattered light shows the differences in the condition of the GaAs surface. Figure 5 clearly shows that the electrode surface becomes smoother with a higher scan rate.

In the third region, the \( \Delta R/R \) value increased with the charge corresponding to the electrodeposition of \( \text{Cu} \) and the scattered light intensity slightly increased, indicating that the surface roughness became nearly constant. These results suggest that in this region the diffusion layer of \( \text{Cu}^{2+} \) on the \( \text{Cu} \) clusters overlap each other with the growth of the \( \text{Cu} \) clusters. As a result of the overlap of the diffusion layers, the diffusion of the \( \text{Cu}^{2+} \) ion is available only in the \( z \)-direction and the growth mode of the \( \text{Cu} \) clusters changed from three dimensional to one dimensional (\( z \)-direction). Thus, in this region, the thickness of the \( \text{Cu} \) layer increased with the deposition, but the roughness of the electrode surface only slightly changed. Moreover, the independence of the \( \Delta R/R/\text{charge ratio vs. scan rate indicates that the thickness of the Cu layer increased at all scan rates in the same manner in this region.}

Before the electrochemical dissolution of the deposited \( \text{Cu} \) started, the scattered light intensity increased, indicating an increase in the surface roughness. At the beginning of the electrochemical dissolution, i.e., at the potential where the anodic current started to flow, the scattered light intensity still increased, indicating that the electrochemical dissolution of the deposited \( \text{Cu} \) proceeded with the nucleation and growth process. Furthermore, the scattered light intensity returns to the original value at the top of the oxidation peak for \( \text{Cu} \) dissolution, showing that the dissolution process proceeds along with the nucleation process and produces a leveling process. Otherwise, the scattered light intensity must be constant during the dissolution process.

Deposition on the \( \text{(NH}_4\text{)}_2\text{S-treated GaAs surface.} \)---Figure 6 shows the potential dependencies of the current, the \( \Delta R/R \) value, and the scattered light intensity at the \( \text{(NH}_4\text{)}_2\text{S-treated GaAs(001) surface at the scan rate of 5 mV s}^{-1} \). One should note that the scattered light intensity is not directly comparable to the results of the bare electrode because the relative position of the electrode and the detector were not exactly the same. The characteristics of the cyclic voltammograms and the potential dependence of the scattered light intensity obtained at the \( \text{(NH}_4\text{)}_2\text{S-treated surface were almost the same as those at the bare surface. Although the potential dependence of the } \Delta R/R \text{ value was apparently different from that at the bare surface, the essential feature was the same. The apparent difference was caused by the relatively small increase in the } \Delta R/R \text{ value during the deposition while the limiting current was flowing. This similarity can be more clearly seen in the charge dependencies of the } \Delta R/R \text{ value and scattered light intensity shown in Fig. 5e.}

The \( \Delta R/R \) value and the scattered light intensity linearly decreased and increased, respectively, with the charge in region II, and the \( \Delta R/R \) value linearly increased while the scattered light intensity
increased rather slowly with the charge in region III, as was the case at the bare surface. The total charge passed during the deposition was, however, only half that on the bare surface, resulting in a relatively small increase of $\Delta R/R$. The smaller charge is due to the lower current. These results suggest that although the growth process of Cu clusters formed at the (NH$_4$)$_2$S surface was similar to that at the bare surface, the number of clusters formed on the (NH$_4$)$_2$S-modified surface was less than those on the bare surface. Since the Cu deposition on p-GaAs, i.e., the cathodic process at a p-type semiconductor, in the dark can take place through surface states, the (NH$_4$)$_2$S treatment led to a decrease in the Cu deposition rate as a result of the reduction of the defect site that functions as the deposition site.

To confirm the reduction of the defect site by the (NH$_4$)$_2$S treatment, in situ electrochemical AFM measurements were carried out. Figure 7 shows the AFM images of the (a) bare and (b) (NH$_4$)$_2$S-treated GaAs(001) after 30 s of Cu deposition at $-100$, $-250$, and $-450$ mV. At $-100$ mV, which is slightly more negative than the redox potential of Cu$^{2+}$/Cu, only some large Cu clusters were observed on both the surfaces. At $-250$ mV, the number of Cu clusters is greater than that at $-100$ mV on both surfaces. It is clear that the number of clusters formed on the (NH$_4$)$_2$S-treated surface is about half that on the bare surface. At $-450$ mV, the (NH$_4$)$_2$S-treated surface is smoother than the bare surface, supporting the above-mentioned results obtained by the optical measurements.

Thus, the essential feature of the Cu deposition process on the (NH$_4$)$_2$S-treated surface was almost the same as that on the bare electrode. The number of surface defects that work as absorption sites decreased to nearly half that of the bare surface by the (NH$_4$)$_2$S treatment, which is known to decrease the surface defects determined by the photoluminescence intensity measurement.$^{19}$

**Conclusions**

Cu electrodeposition on bare and (NH$_4$)$_2$S-treated p-GaAs(001) surfaces was investigated by measurement of the potential dependence of the current, $\Delta R/R$, and scattered light intensity during the potential scan and in situ electrochemical AFM. Reflectance and light-scattering measurements showed that on both the bare and (NH$_4$)$_2$S-treated surfaces, Cu deposition occurred in a cluster growth mode and the Cu clusters grew in the z-direction at a relatively negative potential where the limiting current was observed. The potential dependencies of the reflectance and scattered light intensity obtained at various scan rates showed that the size of the Cu cluster was smaller at the higher scan rate. The charge due to the Cu deposition at the (NH$_4$)$_2$S-treated surface was nearly half that at the bare surface, and the AFM images showed a decrease in the number of Cu clusters, indicating that the (NH$_4$)$_2$S treatment reduced the defect sites on the surface. As a result, the (NH$_4$)$_2$S treatment provided more uniform Cu/GaAs(001) interfaces in the large overpotential region.

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