HOKKAIDO UNIVERSITY

Title	In Situ Optical and Electrochemical AFM Monitoring of Cu Electrodeposition Process on Bare and (NH4)2S-Treated p-GaAs(001) Surfaces
Author(s)	Tamura, Kazuhisa; Kondo, Toshihiro; Uosaki, Kohei
Citation	Journal of The Electrochemical Society, 147(9), 3356-3360 https://doi.org/10.1149/1.1393906
Issue Date	2000
Doc URL	https://hdl.handle.net/2115/50236
Rights	© The Electrochemical Society, Inc. 2000. All rights reserved. Except as provided under U.S. copyright law, this work may not be reproduced, resold, distributed, or modified without the express permission of The Electrochemical Society (ECS). The archival version of this work was published in J. Electrochem. Soc. 2000 volume 147, issue 9, 3356-3360.
Type	journal article
File Information	JES147-9_3356-3360.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP



Journal of The Electrochemical Society

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

Kazuhisa Tamura, Toshihiro Kondo and Kohei Uosaki

J. Electrochem. Soc. 2000, Volume 147, Issue 9, Pages 3356-3360.
doi: 10.1149/1.1393906

Email alerting service Receive free email alerts when new articles cite this article - sign up in the box at the top right corner of the article or click here

To subscribe to *Journal of The Electrochemical Society* go to:
http://jes.ecsdl.org/subscriptions

© 2000 ECS - The Electrochemical Society

Downloaded on 2012-09-26 to IP **133.87.26.18** address. Redistribution subject to ECS license or copyright; see **www.esltbd.org**

Journal of The Electrochemical Society, **147** (9) 3356-3360 (2000)
S0013-4651(00)01-121-6 CCC: $7.00 © The Electrochemical Society, Inc.

In Situ Optical and Electrochemical AFM Monitoring of Cu Electrodeposition Process on Bare and $(NH_4)_2S$-Treated p-GaAs(001) Surfaces

Kazuhisa Tamura, Toshihiro Kondo, and Kohei Uosaki*,z

Physical Chemistry Laboratory, Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

The initial process of Cu electrodeposition on bare and $(NH_4)_2S$-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 $(NH_4)_2S$-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 $(NH_4)_2S$-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 $(NH_4)_2S$-treated surfaces, suggesting a reduction in the defect sites by the $(NH_4)_2S$ treatment.
© 2000 The Electrochemical Society. S0013-4651(00)01-121-6. All rights reserved.

Manuscript submitted January 28, 2000; revised manuscript received May 22, 2000.

The metal/semiconductor interface is one of the basic key components in electronic devices and has been the subject of significant scientific interest. GaAs is recognized as one of the most important semiconductor materials because of its high electron mobility, which is essential for processing high-frequency signals. Thus, metal deposition on GaAs has been investigated in various aspects by using many techniques and the electrochemical deposition of Cu on GaAs has been studied by many research groups. Vereecken *et al.* reported that on n- and p-GaAs(001) electrodes, Cu^{2+} was reduced to Cu^{+} before the reduction to Cu^{0} in a solution containing the chloride anion, but no Cu^{+} intermediate was detected on n- and p-GaAs(001) electrodes in a solution containing sulfate ion.[1,2] Scherb and Kolb followed the electrochemical deposition process of Cu in the presence of a side reaction by photoreflectivity measurements.[3] We have found that the randomly distributed Cu clusters were formed on a p-GaAs(001) surface in a solution containing chloride or sulfate ion by using *in situ* electrochemical atomic force microscopy (AFM). [4-6] Smilgies *et al.* showed that the <100> direction of the deposited Cu was aligned with the <110> direction of the n-GaAs(001) surface by using X-ray diffraction.[7] We also found that Cu nanoclusters with a shorter Cu-Cu distance than that of the bulk Cu were formed during an early stage of Cu electrochemical deposition on a p-GaAs(001) electrode by using *in situ* surface extended X-ray absorption fine structure (EXAFS). [8,9] Scherb *et al.* examined the structure of the Cu deposition in n- and p-GaAs(001) by X-ray standing waves. [10] Although these results provided detailed information about the microscopic structures of the deposits, *i.e.*, atomic level structure, they did not give the information about the deposition process in a macroscopic sense, *i.e.*, thickness of deposit and morphology of the electrode surface, which are also important for understanding the deposition process. It was demonstrated that reflectance and light-scattering measurements are convenient real-time methods for evaluating the thickness of thin films formed on electrodes and the surface roughness of the electrodes, respectively. [3,11] Thus, the simultaneous measurement of the reflectance and light scattering should provide detailed macroscopic information about the surface structure of the electrode during the deposition process.

It is well known that GaAs has many surface states, which is the major reason for the Fermi level pinning and poor thermionic emission characteristics. [12] To reduce the density of the surface states, surface treatments have been extensively investigated. [13-18] Sik *et al.* reported that the surface treatment with $(NH_4)_2S$ solution gave oxide-free surfaces with few surface states. [19] Sandrof *et al.* found the formation of As_xS_y chemical bonds using X-ray photoelectron spectroscopy (XPS). [20] Maeyama *et al.* determined the surface structure of the $(NH_4)_2S$-treated surface by EXAFS. [21] It was shown that the $(NH_4)_2S$ treatment improved the capacitance-voltage characteristics of a GaAs-based metal-insulator-semiconductor device. [22]

In this paper, the initial process of Cu electrodeposition on bare and $(NH_4)_2S$-treated surfaces was investigated by simultaneous reflectance and light-scattering measurements. These results indicate that on both the bare and $(NH_4)_2S$-treated surfaces, Cu deposition initially occurred in the Volmer-Weber growth mode and the Cu clusters then grew in the *z*-direction at a relatively negative potential where the limiting current was observed. These measurements also showed that the $(NH_4)_2S$ treatment lead to a reduction in the surface defects, which was confirmed by *in situ* AFM.

Experimental

Reagent-grade H_2SO_4, $CuSO_4$, and ethanol were obtained from Wako Pure Chemicals and used without further purification. Water was purified using a Milli-Q water purification system (Yamato, WQ-500).

Single crystalline Zn-doped p-GaAs(001) wafers (Mitsubishi Chemical Corp., doping density 1.0×10^{19} cm^{-3}) were used as the electrodes. The wafers were cleaned in hot ethanol, dipped in 3 M HCl to remove the surface oxide, and then rinsed with pure water. The $(NH_4)_2S$ treatment was carried out by immersing the sample for 30 min in the $(NH_4)_2S$ solution at 90°C.[19] Ohmic contact was secured using an InZn alloy. The GaAs sample was fixed on a sample holder, which was made from polytetrafluoroethylene (PTFE), and then placed in a photoelectrochemical cell, which was made from Pyrex with an optically flat window. The electrode potential was controlled by a potentiostat (Hokuto Denko, HA151) and a function generator (Hokuto Denko, HB-111) with respect to the Ag/AgCl electrode (1 M KCl). The counter electrode was a Pt wire.

Reflectance and light-scattering measurements were carried out by using a 10 mW He-Ne laser as the light source and Si photodiodes as detectors. Si photodiodes were placed in the reflected light path and next to the optical window for the reflectance and light-scattering measurements. The incident angle of the laser beam was *ca*. 80° and the polarization was perpendicular to the surface. The output of the Si photodiodes was captured by a computer through a 12 bit analog/digital (A/D) converter. The normalized reflectance change ($\Delta R/R$) is defined as

$$\frac{\Delta R}{R} = \frac{R(E) - R_0}{R_0} \quad [1]$$

* Electrochemical Society Active Member.
z E-mail: uosaki@pcl.sci.hokudai.ac.jp

Downloaded on 2012-09-26 to IP 133.87.26.18 address. Redistribution subject to ECS license or copyright; see www.esltbd.org

S0013-4651(00)01-121-6 CCC: $7.00 © The Electrochemical Society, Inc.

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.[4]

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 H_2SO_4 solution containing 1 mM $CuSO_4$ when the potential was scanned between +0.1 and −0.49 V at various sweep rates. The scattered light intensity was reported with respect to that at +0.1 V.

When the potential was scanned from +0.1 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 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 V, the $\Delta R/R$ and the scattered light intensity started to decrease and increase sharply, respectively. At *ca.* −0.24 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 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 V where the cathodic current still flowed, the $\Delta R/R$ value became constant and the scattered light intensity started to increase. The current became anodic at *ca.* −0.09 V. As the potential became more positive, the $\Delta R/R$ value and the scattered light intensity started to rapidly decrease. The $\Delta R/R$ 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.

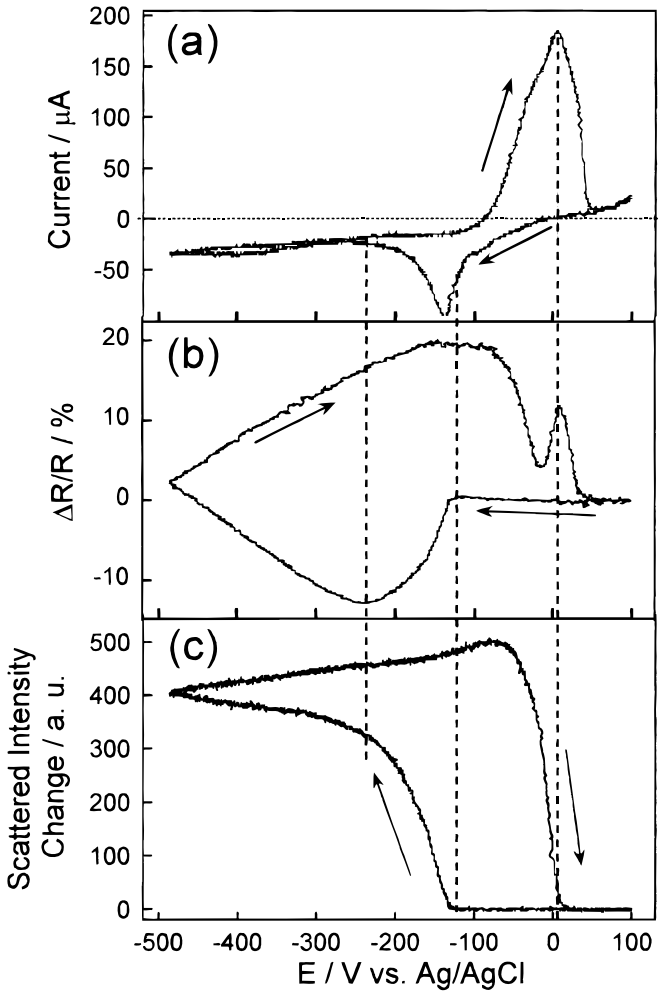


Figure 1. (a) Cyclic voltammogram, (b) $\Delta R/R$, and (c) scattered light intensity of p-GaAs(001) electrode in 0.1 M H_2SO_4 solution containing 1 mM $CuSO_4$. Sweep rate 2 mV s^{-1}.

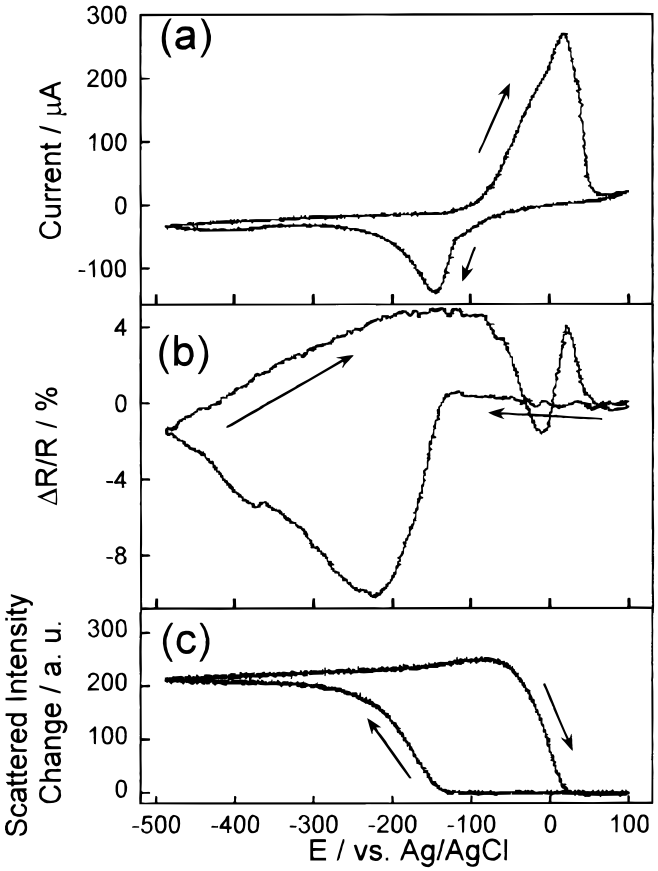


Figure 2. (a) Cyclic voltammogram, (b) $\Delta R/R$, and (c) scattered light intensity of p-GaAs(001) electrode in 0.1 M H_2SO_4 solution containing 1 mM $CuSO_4$. Sweep rate 5 mV s^{-1}.

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

Downloaded on 2012-09-26 to IP 133.87.26.18 address. Redistribution subject to ECS license or copyright; see www.esltbd.org

S0013-4651(00)01-121-6 CCC: $7.00 © The Electrochemical Society, Inc.

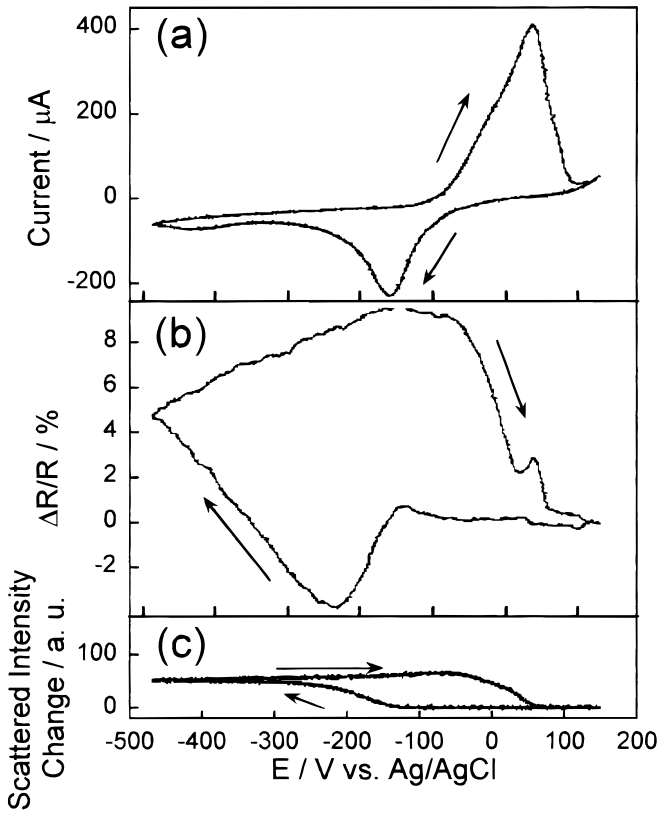


Figure 3. (a) Cyclic voltammogram, (b) $\Delta R/R$, and (c) scattered light intensity of p-GaAs(001) electrode in 0.1 M H_2SO_4 solution containing 1 mM $CuSO_4$. Sweep rate 10 mV s^{-1}.

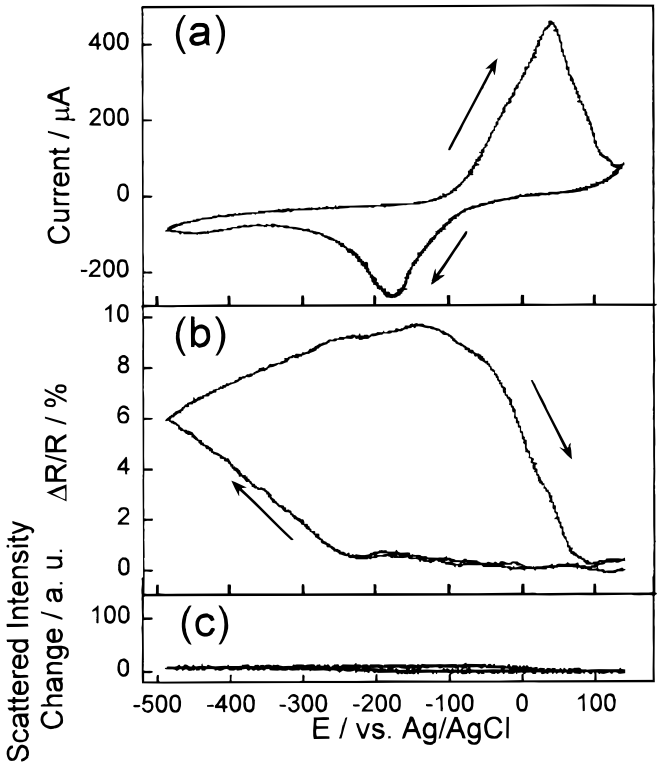


Figure 4. (a) Cyclic voltammogram, (b) $\Delta R/R$, and (c) scattered light intensity of p-GaAs(001) electrode in 0.1 M H_2SO_4 solution containing 1 mM $CuSO_4$. Sweep rate 20 mV s^{-1}.

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, λ, $\Delta R/R$ is given by[23]

$$\frac{\Delta R}{R} = \frac{8\pi d\sqrt{\epsilon_1}\cos\varphi}{\lambda} Im\left(\frac{\hat{\epsilon}_2 - \hat{\epsilon}_3}{\epsilon_1 - \hat{\epsilon}_3}\right) \quad [2]$$

where φ is the incident angle, ϵ_1 is the dielectric constants of the electrolyte, and $\hat{\epsilon}_2$ and $\hat{\epsilon}_3$ are the complex dielectric constants of the film and the substrate, respectively. $\hat{\epsilon}$ is given by

$$\hat{\epsilon} = \epsilon' - i\epsilon'' \quad [3]$$

where ϵ' and ϵ'' 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.

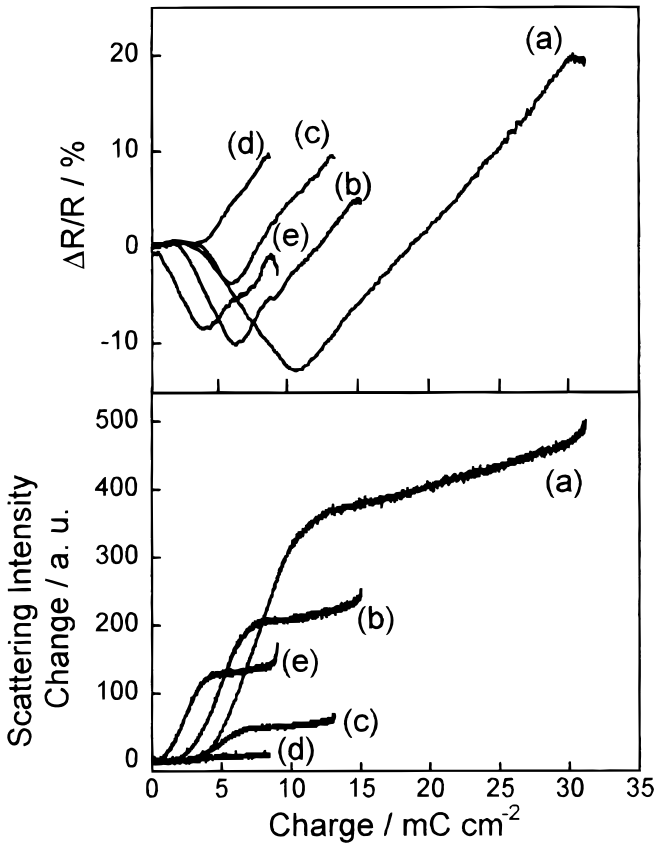


Figure 5. Coverage dependence of $\Delta R/R$ (top) and scattered light intensity (bottom) of (a-d) p-GaAs(001) and (e) $(NH_4)_2S$-treated GaAs electrode in 0.1 M H_2SO_4 solution containing 1 mM $CuSO_4$. Sweep rate are (a) 2, (b) 5, (c) 10, (d) 20, and (e) 5 mV s^{-1}.

Downloaded on 2012-09-26 to IP 133.87.26.18 address. Redistribution subject to ECS license or copyright; see www.esltbd.org

S0013-4651(00)01-121-6 CCC: $7.00 © The Electrochemical Society, Inc.

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

$$I = \frac{\pi^2}{2}(1 + \cos\theta)\frac{cNV^2}{\epsilon_0^2 r^2 \lambda^4} I_0 \quad [4]$$

where θ is the scattering angle, *N* is the number of the scatterers, *V* is the volume of the scatterers, ϵ_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 Cu^{2+} to 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 Cu, and a simulation of the Δ*R*/*R* for the electrolyte/Cu/GaAs three-phase system based on Eq. 2 showed that the Δ*R*/*R* value increases with the thickness of Cu.[23] In the first region, however, the Δ*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 Cu deposition, *e.g.*, the electrochemical reduction of surface oxides on GaAs such as As_2O_3, As_2O_5, and/or Ga_2O_3 [19] took place. A simulation of the Δ*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 Δ*R*/*R* value increases if the surface oxide is removed. In the present result, the Δ*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 Δ*R*/*R* value in the first region was *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 Cu started and the cathodic current sharply increased (second region). In this region, the scattered light intensity increased, and the Δ*R*/*R* value decreased as the electrodeposition of Cu proceeded. The decrease in the Δ*R*/*R* value should be caused by the increase in the scattered light, which reflects the increase in the surface roughness. Thus, Cu clusters grew mainly in size not in number with the increase in the amount of electrodeposited Cu. These results support our previous results that 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 Δ*R*/*R* value increased with the charge corresponding to the electrodeposition of 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 Cu^{2+} on the Cu clusters overlap each other with the growth of the Cu clusters. As a result of the overlap of the diffusion layers, the diffusion of the Cu^{2+} ion is available only in the *z*-direction and the growth mode of the Cu clusters changed from three dimensional to one dimensional (*z*-direction). Thus, in this region, the thickness of the Cu layer increased with the deposition, but the roughness of the electrode surface only slightly changed. Moreover, the independence of the (Δ*R*/*R*)/charge ratio *vs.* the 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 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 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 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 $(NH_4)_2S$-treated GaAs surface.—Figure 6 shows the potential dependencies of the current, the Δ*R*/*R* value, and the scattered light intensity at the $(NH_4)_2S$-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 $(NH_4)_2S$-treated surface were almost the same as those at the bare surface. Although the potential dependence of the Δ*R*/*R* 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 Δ*R*/*R* value during the deposition while the limiting current was flowing. This similarity can be more clearly seen in the charge dependencies of the Δ*R*/*R* value and scattered light intensity shown in Fig. 5e.

The Δ*R*/*R* value and the scattered light intensity linearly decreased and increased, respectively, with the charge in region II, and the Δ*R*/*R* value linearly increased while the scattered light intensity

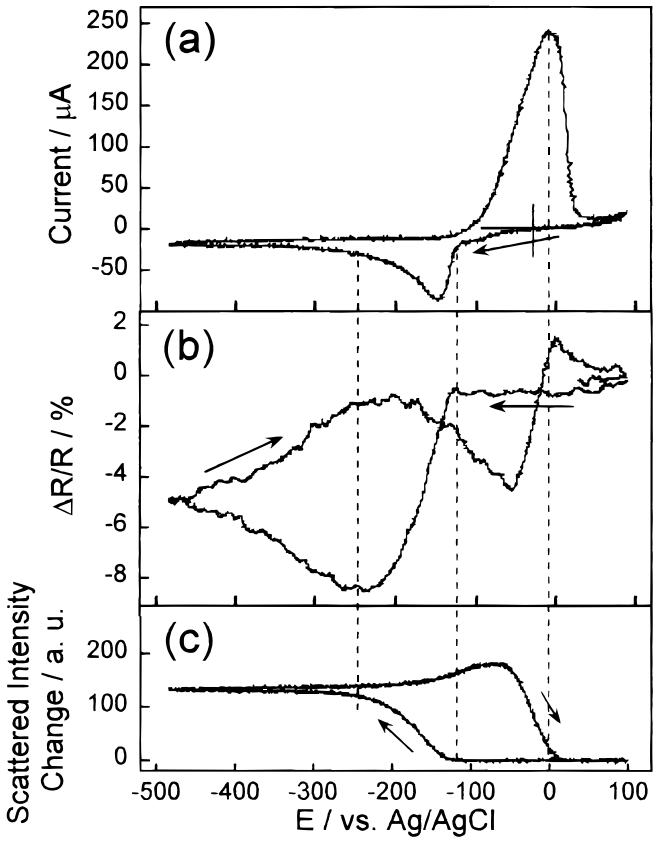


Figure 6. (a) Cyclic voltammogram, (b) Δ*R*/*R*, and (c) scattered light intensity of $(NH_4)_2S$-treated p-GaAs(001) electrode in 0.1 M H_2SO_4 solution containing 1 mM $CuSO_4$. Sweep rate 5 mV s^{-1}.

Downloaded on 2012-09-26 to IP 133.87.26.18 address. Redistribution subject to ECS license or copyright; see www.esltbd.org

S0013-4651(00)01-121-6 CCC: $7.00 © The Electrochemical Society, Inc.

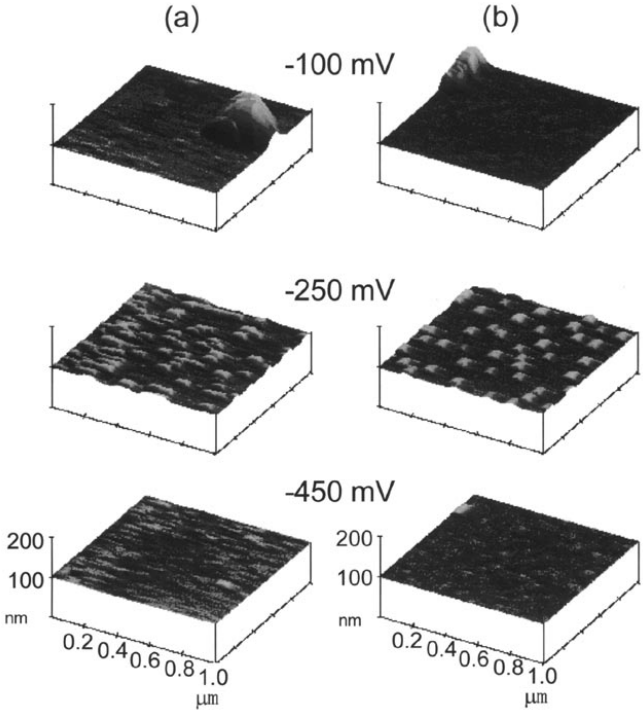


Figure 7. AFM images of (a) bare and (b) $(NH_4)_2S$-treated p-GaAs(001) electrode in 0.1 M H_2SO_4 solution containing 1 mM $CuSO_4$ obtained 30 s after the potential of −100 mV (top), −250 mV (middle), and −450 mV (bottom) were applied.

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 $(NH_4)_2S$ surface was similar to that at the bare surface, the number of clusters formed on the $(NH_4)_2S$-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 $(NH_4)_2S$ 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 $(NH_4)_2S$ treatment, *in situ* electrochemical AFM measurements were carried out. Figure 7 shows the AFM images of the (a) bare and (b) $(NH_4)_2S$-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 $(NH_4)_2S$-treated surface is about half that on the bare surface. At −450 mV, the $(NH_4)_2S$-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 $(NH_4)_2S$-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 $(NH_4)_2S$ treatment, which is known to decrease the surface defects determined by the photoluminescence intensity measurement.[19]

Conclusions

Cu electrodeposition on bare and $(NH_4)_2S$-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 $(NH_4)_2S$-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 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 $(NH_4)_2S$-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 $(NH_4)_2S$ treatment reduced the defect sites on the surface. As a result, the $(NH_4)_2S$ treatment provided more uniform Cu/GaAs(001) interfaces in the large overpotential region.

Acknowledgment

We are grateful to H. Fujita and H. Fujisawa of the Mitsubishi Chemical Corporation for providing us with the GaAs single crystals. This work was partially supported by Grants-in-Aid for Scientific Research on Priority Area of "Electrochemistry of Ordered Interface" (no. 09237101) from the Ministry of Education, Science, Sports and Culture, Japan.

Hokkaido University assisted in meeting the publication costs of this article.

References

1. P. M. Vereecken, F. V. Kerchove, and W. P. Gomes, *Electrochim. Acta*, **41**, 95 (1996).
2. P. M. Vereecken, K. Strubbe, and W. P. Gomes, *J. Electrochem. Soc.*, **145**, 3075 (1998).
3. G. Scherb and D. M. Kolb, *J. Electroanal. Chem.*, **396**, 151 (1995).
4. M. Koinuma and K. Uosaki, *Electrochim. Acta*, **40**, 1345 (1995).
5. M. Koinuma and K. Uosaki, *Surf. Sci.*, **375-358**, 565 (1996).
6. M. Koinuma and K. Uosaki, *J. Electroanal. Chem.*, **409**, 45 (1996).
7. D. M. Smilgies, R. Feidenhans'l, G. Scherb, D. M. Kolb, A. Kazimirov, and J. Zegenhagen, *Surf. Sci.*, **367**, 40 (1996).
8. K. Uosaki, T. Kondo, M. Koinuma, K. Tamura, and H. Oyanagi, *Appl. Surf. Sci.*, **121-122**, 102 (1997).
9. T. Kondo, K. Tamura, M. Koinuma, H. Oyanagi, and K. Uosaki, *Chem. Lett.*, 761 (1997).
10. G. Scherb, A. Kazimirov, J. Zegenhagen, T. L. Lee, M. J. Bedzyk, H. Noguchi, and K. Uosaki, *Phys. Rev. B*, **58**, 10800 (1998).
11. K. L. Kavanagh, R. S. Goldman, C. Lavoie, B. Leduc, T. Pinnington, T. Tiedje, D. Klug, and J. Tse, *J. Cryst. Growth*, **174**, 550 (1997).
12. N. Wu, T. Hashizume, and H. Hasegawa, *Jpn. J. Appl. Phys. Part 1*, **33**, 936 (1994).
13. K. Matsushita, N. Suzuki, S. Okuyama, and Y. Kumagai, *Jpn. J. Appl. Phys. Part 1*, **35**, 5293 (1996).
14. V. N. Bessolov, E. V. Konenkova, and M. V. Lebedev, *J. Vac. Sci. Technol. B*, **14**, 2761 (1996).
15. C. H. Chung, S. I. Yi, and W. H. Weinberg, *Appl. Phys. Lett.*, **69**, 3369 (1996).
16. S. Nozaki, S. Tamura, and K. Takahashi, *J. Vac. Sci. Technol. B*, **13**, 297 (1995).
17. B. A. Kruvilla, A. Datta, G. S. Shekhawat, A. K. Sharma, P. D. Vyas, R. P. Gupta, and S. K. Kulkarni, *Appl. Phys. Lett.*, **69**, 415 (1996).
18. M. G. Kang, H. H. Park, K. S. Shu, and J. L. Lee, *Thin Solid Films*, **290-291**, 328 (1996).
19. H. Sik, Y. Feurprier, C. Cardinaud, G. Turban, and A. Scavennec, *J. Electrochem. Soc.*, **144**, 2106 (1997).
20. C. J. Sandroff, M. S. Hegde, and C. C. Chang, *J. Vac. Sci. Technol. B*, **7**, 841 (1989).
21. S. Maeyama, M. Suginama, and M. Oshima, *Surf. Sci.*, **357-358**, 527 (1996).
22. J. F. Fan, H. Oigawa, and Y. Nannichi, *Jpn. J. Appl. Phys.*, **27**, 761 (1988).
23. D. M. Kolb, in *Spectroelectrochemistry*, R. B. Gale, Editors, p. 87, Plenum Press, New York (1988).
24. L. Rayleigh, *Proc. R. Soc. London, Ser. A*, **84**, 25 (1911).
25. D. E. Aspnes, G. P. Schwartz, G. J. Gualtieri, A. A. Studna, and B. Schwartz, *J. Electrochem. Soc.*, **128**, 590 (1981).
26. A. M. Kaminska and M. Guziewicz, *Thin Solid Films*, **254**, 194 (1995).

Downloaded on 2012-09-26 to IP 133.87.26.18 address. Redistribution subject to ECS license or copyright; see www.esltbd.org