

Sudden beginning of metallic behavior at Ag/Si(100) interface: A real-time photoreflectance-spectroscopy investigation

Y. Borensztein, R. Alameh, and M. Roy

Laboratoire d'Optique des Solides, Université Pierre et Marie Curie-Case 80, 4, place Jussieu, 75252 Paris Cedex 05, France

(Received 16 July 1993)

The Ag growth of Si(100)-2×1 has been investigated by real-time *in situ* photoreflectance spectroscopy, in the spectral range 1.1–5.4 eV. For the lowest coverages, the interface displays a nonmetallic character, due to the covalent bonding between the Ag atoms and the Si atoms. When the Ag coverage increases, the additional deposits become suddenly metallic and the differential reflectance spectra display typical features: rapid increase of the signal in the red and near-infrared range because of the optical response of the conduction electrons; appearance and growing of a plasma resonance in the thin Ag deposits. Moreover, the following of the signal during the Ag growth permits accurate determination of the beginning of the metallic behavior.

The determination of the metallization of surfaces of semiconductors is an important goal, as well for applications like the fabrication of microelectronics devices as for fundamental interest, like comprehension of the Schottky barrier formation. However, the distinction between metallic and nonmetallic behavior of the interface at the early stage of metal deposits is not easy. For example, photoemission spectroscopy cannot give easily a clear answer in the initial growth of metal on a semiconductor, in particular for *s*-electron metals, because of their small cross section with the ultraviolet photons.^{1,2} High-resolution electron energy-loss spectroscopy has been already used to observe the metallization of metal overlayers.¹ However, its necessary high-vacuum environment, its cost, and the time required for data accumulation make it a weighty technique. *In situ* dc conductivity measurements have been performed also,³ but provide information which does not concern the microscopic metallic character of the adlayer, but its macroscopic conductivity, i.e., the existence or not of continuous conducting circuits at the surface.

We propose in this paper an alternative method in order to determine the metallic character of a metal overlayer on a semiconductor surface, which is based on real-time differential photoreflectance spectroscopy. We present the results of an investigation of Ag growth on Si(100)-2×1 surface, which can be considered as a model system because of the low interaction of Ag with Si and of its abrupt interface. The optical measurement is indeed a powerful tool for the discrepancy between metallic and nonmetallic character of an interface or of an adlayer involving metal atoms with *s* electrons, as will be seen below. We also demonstrate the sudden appearance of metallic behavior with increasing Ag coverage.

The photoreflectance measurements were performed by means of a rapid surface reflectance spectrometer, based on an optical multichannel analyzer (OMA) constituted by a 1024 Si-photodiode array. The measured quantity is the differential reflectance (DR), which is the relative change of the reflectance of the sample upon Ag adsorption: $\Delta R/R = (R_{\text{Ag/Si}} - R_{\text{Si}})/R_{\text{Si}}$, where R_{Si} is the

reflectance of the bare Si(100)-2×1 surface and $R_{\text{Ag/Si}}$ the reflectance of the same surface covered by the Ag deposits. The energy range covered was 1.5–5.5 eV. Rapid scans could be performed on all the spectral range by using the OMA, so that each spectrum could be obtained in a few seconds, after several accumulations of the data in order to improve the signal-to-noise ratio. This allowed us to perform real-time spectroscopic measurements during the growth of Ag, which was deposited at a rate of 0.1 monolayer/min, where the monolayer (ML) corresponds to the number of atoms of the first Si layer of the substrate, i.e., to 6.8×10^{14} atoms/cm². More details of the experimental setup can be found elsewhere.⁴ The amounts of Ag deposits were monitored by a quartz microbalance which had been previously calibrated by grazing-incidence x-ray reflectometry. The absolute accuracy of the deposit amounts was estimated to be a few hundredths of a ML. The Si(100) substrate, cut from a phosphorus-doped wafer, was cleaned by heating during 5 min at 850 °C and slowly cooled down, in order to get a sharp 2×1 pattern in low-energy-electron-diffraction observation.

Figure 1 presents the experimental DR spectra directly measured for various Ag coverages θ . For two lower coverage curves, the main features is a maximum of DR centered at about 2.3 eV with a width of 1.5 eV, increasing with the amount of Ag. This structure, due to an optical absorption at the Ag-Si interface, has been identified as an electronic transition involving electronic interface states related to the ionocovalent Ag-Si bonds.⁵ A similar feature has been obtained on other Ag/Si interfaces and can therefore be considered as the “optical signature” of the bonding between Ag and Si atoms. In the present experiment, the 2.3-eV absorption is increasing up to a saturation coverage equal to about 0.55–0.6 ML, corresponding to the formation of a low-density intermediate Ag layer, covering a large part of the substrate. The largest coverage curve presented in Fig. 1 corresponds to $\theta=2.96$ ML. The line shape of the curve is quite different from the other ones, and is indicative of the metallic behavior of this Ag deposit. Indeed, the in-

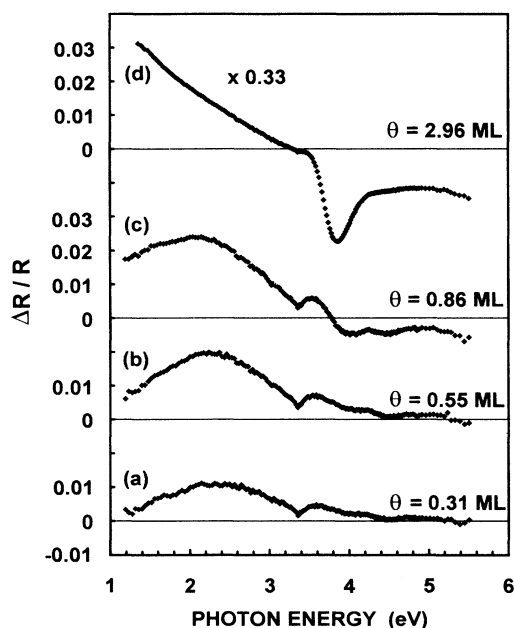


FIG. 1. Differential reflectivity $\Delta R/R$ spectra measured for several Ag coverages θ on Si(100)- 2×1 .

crease of DR for the lower energies, in the red and the near-infrared range, is due to the high reflectance power of thin metallic films, because of the quasifree conduction electrons. Moreover, the deep minimum centered at 3.8 eV is known to be due to a plasma resonance in Ag films.⁶ For the intermediate coverage ($\theta=0.86$ ML), little above the saturation coverage, the situation does not seem so clear. The main feature at 2.3 eV is still present, but one can observe a slight increase of DR for $\hbar\omega < 2$ eV and negative values of DR for $\hbar\omega > 3.7$ eV, which were not present for lower values of θ . One can wonder if this is due to the metallization of the overlayer, as in the larger coverage case.

This question can be answered in Fig. 2, where the changes in DR due to several increases of the Ag deposit amounts are presented. A powerful property of the DR is that, because of the large penetration depth of light, the reflectance signal due to the buried interface is not damped down by thin overlayers, contrary to techniques involving electrons. It is therefore possible to get the contribution of additional deposits to DR simply by differences.⁷ In consequence, Fig. 2 presents the differences $\delta(\Delta R/R)$ between the signals measured for coverages ranging from 0.39 to 2.96 ML. Curve (a) shows that, up to at least $\theta=0.55$ ML, additional Ag deposits mainly increase the optical absorption at 2.3 eV, which indicates that the Ag atoms continue to be bound to the substrate Si atoms. On the other hand, curves (b) and (c), obtained for additional Ag coverages equal to 0.07 and 0.23 ML above $\theta=0.55$ ML, respectively, display a line shape similar to the one of the largest coverage curve (d), obtained for a coverage of 2.41 ML above the 0.55-ML film, due to the metallic character of the de-

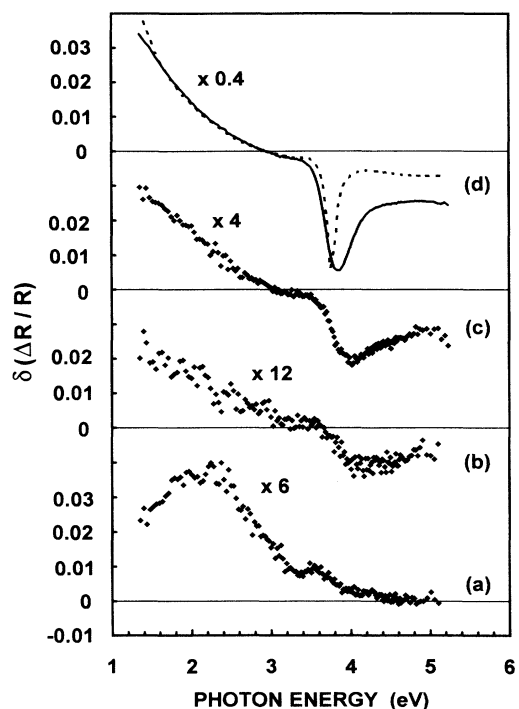


FIG. 2. Contributions to the DR: $\delta(\Delta R/R)$, due to additional successive Ag deposits, obtained by differences between the DR spectra. (a) 0.55–0.39 ML; (b) 0.62–0.55 ML; (c) 0.78–0.55 ML; (d) 2.96–0.55 ML (continuous line, experiment; dashed line, calculation).

posits. We have indeed compared the difference experimental curve (d) with the result of a theoretical calculation using a classical multilayer treatment of the reflectance, where the additional Ag layer has been modeled by flat metallic three-dimensional Ag islands. The better fitting is obtained, when considering the islands as flattened spheroids, for a distribution of the large axis upon small axis ratios which covers the 1-to-50 range. The agreement with the experimental curve is good, especially in the low-energy range. We can conclude that the overlayer corresponding to curve (d) is metallic and constituted of flat Ag islands. The similar line shapes of curves (b) and (c) lead to the same conclusion: the corresponding overlayers are metallic. Moreover, the observation of the plasma resonance around 4.2 eV for the smaller coverage above the $\theta=0.55$ ML low-density overlayer [curve (b)] shows that the additional Ag atoms gather together to form at least 3-ML-thick islands rather than single ML islands. It has been shown indeed that this plasma resonance cannot be observed by photorefectance experiments for Ag continuous films thinner than three (111)Ag compact monolayers (i.e., 0.7 nm), because of the nonlocality of the optical response.^{8,9} In particular, we have shown this effect for the Ag/Si(111)- 7×7 system at low temperature, where the plasma resonance was observed only for coverages larger than $\theta=3.4$ ML, which was interpreted as due to the essentially layer-by-layer mode of growth of Ag in this case.⁹ These results therefore confirm the Stranski-

Krastanov mode of growth of Ag on Si(100)-2×1 at room temperature, previously observed by other techniques.^{10–13} The main differences between the experimental curves and the calculated ones are the shape and the energy position of the plasma resonance around 3.8 eV, which is broadened and shifted to higher energies in the experiments with respect to the calculation. This can be due to two different causes, which will not be discussed in detail here: (1) the small size of Ag islands which induces a shift of the resonance towards larger energy because of the diffuseness of the electron boundary and/or because of quantum size effects;¹⁴ (2) the nonlocality of the optical response of thin islands which broadens and shifts the resonance.¹⁵

On the other hand, the sudden change in the line shape of $\delta(\Delta R/R)$ below and above about 0.55 ML shows that the Ag deposits get suddenly a metallic behavior. This can be better demonstrated by following the changes in the DR for peculiar energies where the metallic character of the overlayer is clearly seen. Figures 1 and 2 have shown that the main differences between the curves corresponding to nonmetallic character ($\theta < 0.55$) and to metallic character ($\theta > 0.6$) are (1) the increase of DR in the red-infrared range ($\hbar\omega < 2$ eV); (2) the appearance of the plasma resonance minimum at 3.8 eV (shifted to above 4 eV for the smaller coverages). Figure 3 presents the values of the DR followed in real time during the Ag deposition, for two photon energies: $\hbar\omega = 1.15$ eV (near infrared) and 4 eV (plasma resonance). Both curves display a linear change with a small slope up to the coverage $\theta = 0.55$ –0.6 ML. For $\hbar\omega = 1.15$ eV, the DR values are first very small and close to zero. It can be shown that, below the Si direct band gap ($\hbar\omega = 3.4$ eV), the DR quantity is proportional to the optical conductivity of the overlayer.¹⁶ Thus, the small values of DR at 1.15 eV show that the optical conductivity of the Ag overlayer is very low, and therefore that the overlayer displays a nonmetallic character. The Ag 5s electrons are indeed rather involved in ionocovalent bonds with the substrate Si atoms than in metallic bonding between Ag atoms. The fact that the values are not strictly zero can be explained by the fact that this energy is not far enough from the 2.3 absorption band. In order to avoid this problem, DR measurements should be performed at lower energies in fairer infrared, but this was not possible with the Si photodiode array used in the present experiments. Then, the slope suddenly changes at $\theta = 0.55$ ML. The rapid increase of the DR above this coverage corresponds to an increase of the optical conductivity and therefore indicates the sudden appearance of the metallic character of the additional Ag deposits. This interpretation is reinforced by following the DR values near the initial plasma resonance energy. For $\hbar\omega = 4$ eV, the DR values are almost zero up to $\theta = 0.6$ ML, then the slope becomes clearly negative. This shows that, for coverages smaller than 0.6 ML, no plasma resonance is observed, while it appears suddenly at $\theta = 0.6$ ML, and then increases progressively. The value $\theta = 0.55$ –0.6 ML for the beginning of the metallic behavior has to be compared to previously proposed values for the saturation coverage of the intermediate layer at room temperature,

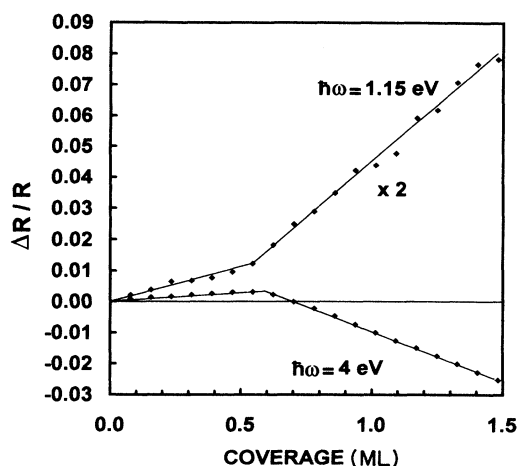


FIG. 3. Changes in the DR for two different photon energies, as a function of the Ag coverage, measured by real-time spectroscopy.

either 0.5 (Ref. 10) or 1 ML.¹³ Our optical experiments have been performed on several Si samples, which led to values of the metallic edge varying between 0.5 and 0.8 ML. We expect that the beginning of the metallic behavior occurs when all the Si dangling bonds are saturated by Ag atoms. It must be noticed that the Si samples used in the present experiments had vicinal surfaces titled 4° towards the [011] direction. It can be seen from scanning tunneling microscopy experiments¹⁷ that this leads to a large amount of steps and missing dimers, yielding a dimer density lower than about 80% of that of the ideal reconstructed surface. The scattering of the values we obtained is therefore probably due to different dimer densities at our substrate surfaces, because of non-perfectly reproducible sample preparing conditions. However, all the values we determined were larger than 0.5 ML, which favors the 1-ML value recently proposed¹³ for a perfect intermediate layer.

In summary, we have shown that at room temperature, the Ag-Si(100) interface is initially nonmetallic, and that the Ag atoms are probably bound to the Si substrate atoms. After the completion of the intermediate layer, the additional Ag atoms gather to form flat three-dimensional islands, and display a metallic behavior due to the delocalization of the *s* conduction electrons within each island. The observation of the plasma resonance indicates that the islands are three-compact-monolayers thick at least. These results demonstrate that differential reflectance spectroscopy is a powerful tool in order to distinguish between nonmetallic and metallic behavior of Ag overlayers on Si. Moreover, the real-time measurements during Ag deposits permits us to determine precisely the appearance of metallic behavior. The Ag/Si system we have studied here can be considered as a model system, but this optical technique could be used to investigate the growth of any other metal on a semiconductor surface, either for *s*-electron metals (alkali metals, noble metals, Al, etc.) or transition metals (for example, for studying

the *in situ* formation of silicides and for determining their semiconducting or metallic character). A more precise determination could be reached by extending the measurements in the middle infrared, where the metallic behavior is better observed. Finally, we notice that this

technique can also be used in nonvacuum environments, like liquids (electrolytes) or gas (reactors).

Laboratoire d'Optique des Solides is UA No. 781 of CNRS.

-
- ¹N. J. DiNardo, T. Maeda Wong, and E. W. Plummer, *Phys. Rev. Lett.* **65**, 2177 (1990).
- ²P. Soukiassian, M. H. Bakshi, Z. Hurych, and T. M. Gentle, *Surf. Sci.* **221**, L759 (1988).
- ³R. Schad, S. Heun, T. Heidenblut, and M. Henzler, *Phys. Rev. B* **45**, 11 430 (1992).
- ⁴Y. Borensztein, T. Lopez-Rios, and G. Vuye, *Appl. Surf. Sci.* **41/42**, 439 (1989).
- ⁵Y. Borensztein and R. Alameh, *Surf. Sci.* **274**, L509 (1992).
- ⁶Y. Borensztein, R. Alameh, T. Lopez-Rios, and W. Q. Zheng, *Vacuum* **41**, 684 (1990).
- ⁷Y. Borensztein, T. Lopez-Rios, and G. Vuye, *Phys. Rev. B* **37**, 6325 (1988).
- ⁸J. K. Sass, S. Stucki, and H. J. Lewerenz, *Surf. Sci.* **68**, 429 (1977).
- ⁹M. Roy, R. Alameh, and Y. Borensztein (unpublished).
- ¹⁰A. Samsavar, T. Miller, and T. C. Chiang, *Phys. Rev. B* **38**, 9889 (1988); A. Samsavar, E. S. Hirschorn, F. M. Leibsle, and T. C. Chiang, *Phys. Rev. Lett.* **63**, 2830 (1989).
- ¹¹A. Brodde, D. Badt, S. Tosch, and H. Neddemeyer, *J. Vac. Sci. Technol. A* **8**, 251 (1990).
- ¹²T. Hashizume, R. J. Hamers, J. E. Demuth, K. Markert, and T. Sakurai, *J. Vac. Sci. Technol. A* **8**, 249 (1990).
- ¹³X. F. Lin, K. J. Wan, and J. Nogami, *Phys. Rev. B* **47**, 13 491 (1993).
- ¹⁴Y. Borensztein, P. De Andres, R. Monreal, T. Lopez-Rios, and F. Flores, *Phys. Rev. B* **33**, 2828 (1986).
- ¹⁵F. Abelès, Y. Borensztein, M. De Crescenzi, and T. Lopez-Rios, *Surf. Sci.* **101**, 123 (1989).
- ¹⁶A. Bagchi, R. G. Barrera, and A. K. Rajagopal, *Phys. Rev. B* **20**, 4824 (1979).
- ¹⁷B. S. Swartzentruber, N. Kitamura, M. G. Lagally, and M. B. Weber, *Phys. Rev. B* **47**, 13 432 (1993).