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Evidence for germanium segregation on thin films of Ag on Ge(111)

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Ag films prepared on Ge(111) at nearly room temperature were studied with high-resolution core-level photoemission spectroscopy. By selectively modifying the sample structure to label surface sites on the Ag film, we unambiguously identified the presence of a small amount of Ge segregating on top on the growing Ag overlayer. The origin and behavior of these segregated atoms and the structure of the overlayer are discussed.

Because of its importance in practical devices and because it is a fundamental and attractive subject, a growing interest has developed in the study of metal overlayers on semiconductors.[1-3] These systems have been studied extensively by many methods.[1] Nevertheless, controversy and confusion remain for many systems. Questions often arise about overlayer morphology, intermixing, and segregation. The film-growth behaviors are commonly probed by core-level photoemission and Auger electron spectroscopy, which determine the average chemical composition of the sample in the near-surface region. It is often found that the substrate signal does not decay exponentially for increasing metal overlayer thickness. This behavior could be the result of a number of different effects: intermixing, surface segregation of the substrate material, three-dimensional growth of the overlayer, or simply the presence of pin holes in the overlayer (due to intrinsic processes, defects in the starting substrate surface, etc.). One cannot easily distinguish among these different possibilities without knowing the exact origin of the signal from the substrate material.

In this paper, we report an experimental investigation of the growth of Ag on Ge(111)-$c(2\times8)$ at nearly room temperature by high-resolution photoemission from the substrate core levels. Core-level binding energies depend on the local atomic environments; thus, high-resolution spectra may contain information about the presence or absence of atoms in inequivalent sites. This effect has been observed in many cases. For example, surface atoms of single crystals generally show binding-energy shifts relative to the bulk atoms.[4] In certain particularly simple instances, different atomic layers could be distinguished in thin overlayers.[5,6] The detection of inequivalent sites is generally not sufficient in itself to distinguish among the different growth behaviors mentioned above. The emphasis of this paper is on the demonstration of a novel approach in which the sample structure is selectively modified to label specific sites. By this technique we were able to identify positively the presence of a very small amount of Ge segregating on top of the growing Ag film on a Ge(111) substrate. We will discuss the implications of our results with regard to the nature of the substrate, the interface, and the overlayer.

The photoemission experiments were carried out using synchrotron radiation from the Tantalus I storage ring of the University of Wisconsin–Madison at Stoughton, Wisconsin. Light from the ring was monochromatized by a three-meter toroidal-grating monochromator. A double-pass cylindrical-mirror analyzer detected electrons emitted from the sample. High-resolution measurements of the Ge 3d core levels were made with a overall resolution of about 0.2 eV. The binding energies were measured relative to the Fermi level E_F determined from the Fermi edge of a gold foil in electrical contact with the sample. The procedure for preparation of the Ge(111) substrate has been described elsewhere.[7] Subsequent *in situ* high-energy electron diffraction (HEED) studies showed the characteristic nominal $c(2\times8)$ reconstruction, with sharp $\frac{1}{8}$-order spots and a low background. Surface cleanliness was confirmed by examination of valence-band photoemission spectra. The spectra were in excellent agreement with previously reported data.[8]

Ag was deposited upon the Ge(111)-$c(2\times8)$ substrates at temperatures between 50° and 80 °C. The rate of deposition (and thus the film thickness) was measured using a quartz-crystal film-thickness monitor. After deposition, we examined the Ag overlayers with HEED. The overlayer exhibited the Ag(111) face with the $[1\bar{1}0]$ direction parallel to the Ge $[1\bar{1}0]$ direction (parallel epitaxy). The HEED patterns were sharp and indicated the presence of fairly flat Ag overlayers. No tilted Ag facets, clusters, or three-dimensional structures were detected. These observations do not rule out the possibility of cracks or pin holes in the Ag film and the presence of small amounts of Ge in and/or on the film. Our HEED results are consistent with previous investigations.[9]

A set of photoemission spectra (dots) of the Ge 3d core levels for clean Ge(111)-$c(2\times8)$, and the Ge(111) surface covered by 5, 10, 15, and 20 monolayers (ML) of Ag are shown in Fig. 1. One ML is defined here as an atomic layer in Ag(111) or 1.38×10^{15} (Ag atoms)/cm^2. These spectra were taken with a photon energy of 70 eV. The corresponding photoelectron escape depth is about 5.5 Å; thus, the spectra contain significant contribution from the surface atoms. The clean Ge(111)-$c(2\times8)$ core-level line shape has been studied in detail before.[10,11] It is known that the line shape consists of three components; these components, obtained by a least-squares fitting procedure described in Ref. 11, and labeled $C1$, $C2$, and S, are indicated in Fig. 1 by dashed curves. The solid curve in Fig. 1 is the result of the fit to the overall line shape. Following Ref. 11, the component S is derived from Ge atoms which are probably only loosely attached to the surface (like, for example, adatoms). The component $C2$ is most likely derived from the atomic layer just below those atoms corresponding to the S component. The $C1$ component is derived from the "bulk," namely, atoms other than those giving rise to the S

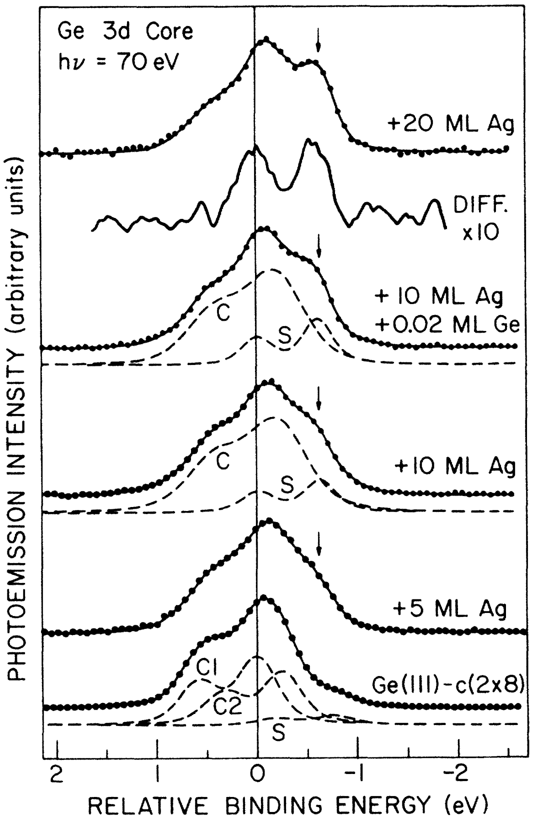

FIG. 1. Ge $3d$ core-level spectra for, from bottom to top, clean Ge(111)-$c(2\times8)$, Ge(111) covered by 5 and 10 ML of Ag, Ge(111) first covered by 10 ML of Ag and then further covered by 0.02 ML of Ge, the difference spectrum between the last two spectra, and Ge(111) covered by 20 ML of Ag. The difference spectrum (magnified 10 times) and its parent spectra are normalized in intensity. The other spectra are shown with arbitrary intensities. Except for the difference spectrum, the dots are the data points, and the solid curves are fits. The dashed curves indicate the components from the fits. The binding-energy scale was referred to 29.42 eV below the Fermi level (the position of the $3d_{5/2}$ core level of the $C1$ contribution to the clean surface fit).

and $C2$ components. In Fig. 1, the background for the spectrum of Ge(111)-$c(2\times8)$ as well as those for the Ag-covered Ge samples has been subtracted for a better presentation of the results. The relative binding-energy scale in Fig. 1 is referred to the binding energy of the $3d_{5/2}$ core level of the $C1$ component (29.42 eV, relative to the Fermi level) of Ge(111).

For increasing amounts of Ag coverage on the Ge surface, the line shape in Fig. 1 changes. The S component, which gives rise to the little bump on the low-binding-energy side of the spectrum for Ge(111)-$c(2\times8)$, disappears after the surface is covered by Ag. A new component, as shown by the shoulder or peak at about a -0.63-eV relative binding energy (indicated in Fig. 1 by the arrows), becomes more pronounced for higher Ag coverages. We follow the same procedure outlined in Ref. 11 for the fitting of the clean spectrum to fit the spectra for Ag-covered Ge, except that we now assume the presence of only two components instead of three, and we allow the more intense, high-binding-energy component to have a wider Gaussian width. This extra Gaussian width was necessary for a good fit, and simulates the effects of small unresolved shifts. An attempt to fit the spectra with three components having the same widths showed that the quality of the fit was not significantly better and the results of the fit were not unique (i.e., too many degrees of freedom). The results of the fit indicated by solid curves are shown in Fig. 1, and the two components C and S are indicated by the dashed curves for 10 ML Ag coverage. The individual components for the other two coverages are not shown here for simplicity.

In our fit, all of the line-shape parameters, including the Gaussian and Lorentzian widths, the branching ratio, and the spin-orbit splitting were unconstrained, yet these quantities all came out to be Ag-coverage independent within close tolerances. The binding energies of the $3d$ core level for different components are shown in Fig. 2. Note that the difference in binding energy between C and S components is constant to within ±20 meV. The absolute binding energies are somewhat uncertain due to errors in the determination of the Fermi-level position for each sample (estimated to be about ±30 meV). Thus, within experimental accuracies, the C and S components have constant binding energies.

The integrated intensities (peak areas) of the Ge $3d$ core-level spectra in Fig. 1 are shown in Table I, together with the intensities for the individual components from the fit. These intensities were expressed in terms of ML; 1 ML of Ge is defined here to correspond to the intensity expected from a Ge(111) double layer or 1.44×10^{15} atoms/cm^2. In this procedure of intensity normalization, we used the usual layer attenuation model and assumed an electron escape depth of 5.5 Å.[11,12] Notice that the C and S components are attenuated at very different rates for increasing Ag coverage, an indication of nontrivial film-growth behavior.

If the Ag overlayer grows in a strictly laminar fashion, the Ge intensity should be negligibly small for 20 ML Ag coverage. Since this is not the case, there may be intermixing, pin holes or cracks in the overlayer, and/or surface segregation of Ge on top of the growing Ag film. On the other hand, the measured intensities indicate that the film has no

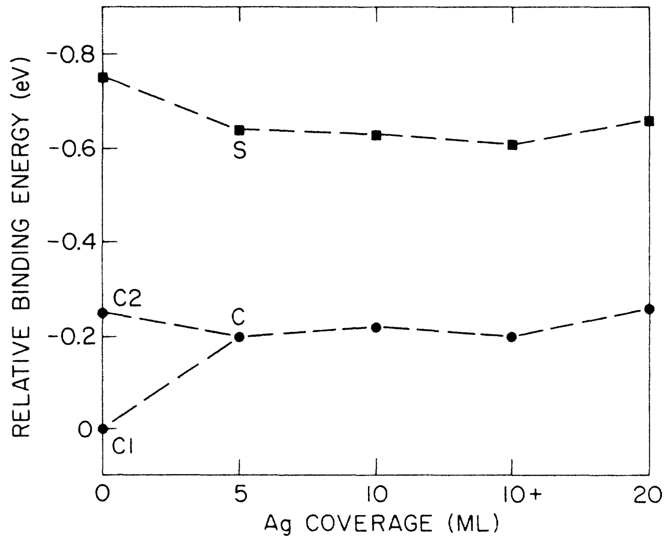

FIG. 2. Relative binding energies of the different components for different sample configurations as indicated. The sample configuration labeled "10+" refers to Ge(111) + 10 ML Ag + 0.02 ML Ge.

TABLE I. Intensities, in ML, or 1.44×10^{15} (Ge atoms)/cm^2. The total intensity is the integrated Ge 3*d* core intensity (peak area) for the sample configurations indicated. The intensities of the core-level line-shape components are obtained from the fits described in the text.

	Ge(111) -$c(2\times8)$	Ge(111) +5 ML Ag	Ge(111) +10 ML Ag	Ge(111) +10 ML Ag +0.02 ML Ge	Ge(111) +20 ML Ag
Total	2.23	0.60	0.31	0.33	0.19
$C1+C2$, C	2.06	0.52	0.25	0.25	0.14
S	0.17	0.08	0.06	0.08	0.05

more than 11% open area over its surface for 10 ML Ag coverage and less at higher coverages. The fact that the *S* component shows a very slow rate of attenuation, as well as the fact that the bulk solubility of Ge in Ag is extremely small at room temperature,[13] immediately suggests that the *S* component corresponds to Ge segregating on top of Ag. To confirm this interpretation, we prepared a sample of Ge covered first by 10 ML of Ag and then further covered by 0.02 ML of Ge. We did not use more Ge to label the surface sites in order to avoid possible Ge-cluster formation leading to complicated, multiple-component shifts. The spectrum for this sample and the results of the fit are shown in Figs. 1 and 2 and Table I. The deposition of Ge only caused the intensity of the *S* component to increase by exactly 0.02 ML, everything else being unchanged. Thus, the *S* component is indeed derived from Ge atoms situated on top of the Ag film. Also displayed in Fig. 1 is the difference spectrum obtained by subtracting the spectrum of Ge + 10 ML Ag from that of Ge + 10 ML Ag + 0.02 ML Ge, which shows the contribution of the added 0.02 ML Ge. This contribution consists of just one spin-orbit-split pair at the same binding energy as that of *S*.

Our interpretation of the results is as follows. The *S* component for the clean surface probably corresponds to loosely attached atoms on the Ge(111)-$c(2\times8)$ surface (such as adatoms). Some or all of these surface atoms have broken loose from the surface and float on top of the growing Ag film. During growth, these segregated Ge atoms can have a finite probability of being buried in the Ag film. From Table I, the disappearance rate of the segregated Ge decreases for increasing Ag coverage, indicating that the disappearance of the segregated Ge is not just due to simple dissolution in the Ag film. This is made possible by the following mechanism. The segregated Ge atoms can form clusters (due to intrinsic processes or the effects of Ag deposition), and presumably the probability of the burial of clusters in the growing Ag overlayer is larger than that for individual atoms. This is because the energy barrier involved in cluster displacement is much larger than that for individual atoms. The clusters, once formed, are likely to be quite stable since the Ge—Ge bond is very strong and the rate of dissolution of Ge in Ag at room temperature is very small.[14] The rate of Ge-cluster formation and the number of clusters decrease for decreasing amounts of segregated Ge on the film surface, thus leading to reduced segregated-Ge burial rates.

From data for samples with lower Ag coverages (not shown here), the component *C* in Fig. 1 can be connected to the *C*1 and *C*2 components of the clean surface. Its intensity as a function of Ag coverage and its binding energy suggest that it is derived from the portion of the Ge substrate where Ag coverage is much less than the average value. These thin spots or pin holes in the Ag film could be intrinsic to the system, a result of domain boundaries or defects likely to occur because of substrate-overlayer lattice mismatch. They could also be induced by extrinsic defects on the starting substrate. This latter interpretation is somewhat unfavorable in view of the fact that all samples that we have experimented with so far show the same behavior. The binding energy of the *C* component is different from the average of those of *C*1 and *C*2 in the clean case, due to a small band bending induced by Ag adsorption.

Bertucci, LeLay, Manneville, and Kern[9] did Auger measurements on the same system. They concluded that the growth mode was layer by layer, based on the attenuation of the substrate signal. Since their measurements were made with a grazing-incidence geometry, we believe that only the very weak *S* component was detected in their experiment at higher coverages due to shadowing effects. With this factor taken into account, our measured intensities are consistent with their values when properly extrapolated.

To summarize, we have performed high-resolution photoemission spectroscopy on Ge 3*d* core levels in thin-film Ag-on-Ge (111) systems. The growth of the overlayer is in parallel epitaxy, but not completely laminar at temperatures below 100 °C. By selectively modifying the sample structure to label surface sites on the overlayer, we show unambiguous evidence for the presence of less than 0.1 ML of Ge atoms segregated on top of the surfaces of these films. These segregated Ge atoms are probably derived from loosely attached Ge atoms on the starting substrate surface. A fraction of them are buried by the growing Ag film. From the burial rate, we estimate the Ge concentration in the Ag film to be on the order of 0.1 at. %. The burial mechanism is likely to be the formation of Ge-atom clusters on the film surfaces followed by their burial by Ag. The films are somewhat leaky, most likely a consequence of lattice mismatch with resulting defects in the overlayer.

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[14] In a separate experiment, we deposited 0.004 ML of Ge on top of a single-crystal Ag(111) sample at room temperature. The Ge core-level intensity did not change as a function of time for over an hour, indicating that the rate of Ge diffusion into Ag is negligible.