

Spectromicroscopic evidence of Ge-GaSe chemical reactions: Not a Schottky system

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Photoelectron-spectromicroscopy experiments unexpectedly revealed a reacted phase for Ge overlayers on GaSe. This finding is in sharp contrast with the notion that this interface is an ideal Schottky system, whose band discontinuities, for example, are determined by the Anderson rule—and with the widespread belief that most III-VI-based interfaces behave like Schottky systems. After this result, to the best of our knowledge, no heterojunction is known that matches the requisites of an ideal Schottky system. [S0163-1829(97)50908-8]

In the course of photoelectron-spectromicroscopy investigations of the band bending of the GaSe-Ge interface, we found an unexpected result: the local Ge $3d$ signal in the region where Ge and GaSe coexist clearly exhibits a reacted component. The line-shape analysis of the Se $3d$ signal also revealed a correlated reacted component, whereas no such component was found for Ga $3d$. Thus, we must conclude that contrary to all previous evidence¹⁻⁴ chemical reactions do occur between the GaSe substrate and the Ge overlayer—and the GaSe-Ge interface is not an ideal Schottky system.^{3,4}

This result is important because of the unique role of III-VI-based systems in the research on semiconductor interfaces.^{1,2,5-8} Metal-semiconductor interfaces are commonly known^{3,4} as “Schottky barriers”; however, their behavior is in most cases very far from that of ideal Schottky metal-semiconductor interfaces, whose energy barrier should be determined by the metal work function.^{3,4} Likewise, most semiconductor-semiconductor heterojunctions strongly deviate from the heterojunction equivalent of the Schottky theory, the Anderson model.⁹

Ideal Schottky systems are in fact extremely rare, bordering nonexistence. For many years, following the work of Williams, McGovern, and their collaborators,⁶⁻⁸ III-VI-based interfaces were thought to provide some of the best examples of such systems, both in the case of metal-semiconductors interfaces⁶⁻⁸ and in the case of heterojunctions.^{1,2} Several published works¹⁻⁸ dealt with this aspect of III-VI-based interfaces, all agreeing on the nonreactive, Schottky-like behavior of many of these systems. This was true, in particular, for the GaSe-Ge heterojunction.¹

Quite recently, the advent of lateral resolution in photoelectron spectroscopy and the corresponding enhancement in analytical capabilities^{10,11} raised some questions about the above, commonly accepted notions. Specifically, Gozzo *et al.* found evidence of lateral variations for both GaSe-metal² and GaSe-Ge interfaces.⁵ Such variations cannot be easily reconciled with a pure Schottky behavior.^{3,4} However, previous experiments did not reveal the most im-

portant piece of evidence against such behavior, which is the evidence of chemical reactions between substrate and overlayer. This evidence directly emerges from our present spectromicroscopy data.

We believe that the key factor in achieving this result was the capability to analyze the chemical properties of the system with high lateral resolution,^{10,11} thereby identifying the reacted species where they exist. Quite significantly, evidence for reacted species was not provided by conventional, space-averaging experiments.¹ Even our own tests with spectromicroscopy at moderate ($\approx 100 \mu\text{m}$) lateral resolution failed to provide the evidence that is instead delivered by the present experiments, for which the lateral resolution was $\approx 0.15 \mu\text{m}$.¹¹

The experiments were performed on the ESCA microscopy undulator beamline¹¹ of the ELETTRA synchrotron light facility, equipped with a spherical grating monochromator. The lateral resolution was the result of the use of a Fresnel zone plate to focus the x-ray beam into a small ($0.15 \times 0.15 \mu\text{m}^2$) spot.¹¹ The electrons emitted from this spot were analyzed using a 100-mm hemispherical analyzer mounted at 70° with respect to the sample, and perpendicular to the incident photon beam. Besides the scanning photoelectron spectromicroscope, the ESCA microscopy beamlines includes facilities for cleaving, thin-film deposition and Auger analysis.

The single-crystal substrates were p -type GaSe $\approx 1 \times 10^{14} \text{cm}^{-3}$ doped with 0.1% As. For this carrier concentration (measured by Hall effect) the Debye length screening was estimated to be $1 \mu\text{m}$, much larger than the photoelectron escape depth. The samples were cleaved *in situ* at a base pressure of 2×10^{-10} Torr, and a nominal 4-ML-thick Ge overlayer was evaporated from a resistively heated W basket; the deposition occurred only on part of the freshly cleaved surface, whereas the rest was screened by a sharp-edged metal shield.

The spectromicroscopy experiments include¹⁰ scanning photoelectron micrographs at selected photoelectron kinetic

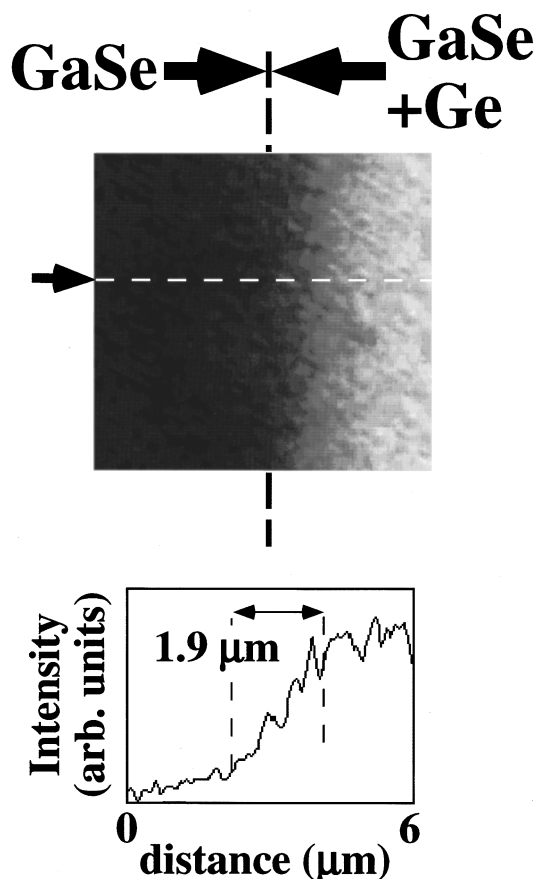


FIG. 1. Top: scanning photoemission microimage of a GaSe substrate partially covered with ≈ 4 ML of Ge, taken for a photon energy of 490 eV and a photoelectron kinetic energy of 459.2 eV, corresponding to the Ge $3d$ signal. The image size is $6.4 \times 6.4 \mu\text{m}$ and the lateral resolution is $0.15 \mu\text{m}$; the brighter zone corresponds to higher Ge emission intensity. Bottom: Ge $3d$ signal intensity profile along the clear dashed line shown in the micrograph at the top. The origin of the coordinates along this line is $1 \mu\text{m}$ to the left of the median point of the intensity profile.

energies, and photoelectron spectra from selected microareas of the sample. In particular, we carefully analyzed spectra taken on several points along lines perpendicular to the separation region between the Ge-covered and Ge-free areas of the surface. This analysis produced the evidence of a reacted phase that constitutes the central point of this paper.

The Ge-covered and Ge-free areas are quite evident in the photoelectron micrograph at the top of Fig. 1, taken at an electron kinetic energy (460 eV) corresponding to the Ge $3d$ signal. Note, however, that the transition between the two areas is not sharp, and it occurs over $\approx 2 \mu\text{m}$. This is revealed not only by the micrograph, but also by the Ge $3d$ intensity profile shown in the bottom part of Fig. 1. The transition width cannot be entirely explained by a penumbra effect of the Ge deposition shield, and we believe that Ge diffusion also plays an important role; this is indicated, for example, by observed variations of the Ge signal intensity over a time scale of tens of minutes.¹²

The transition from the Ge-free to the Ge-covered area is also reflected in the energy positions of the substrate core levels, which change along the clear dashed line shown in the top part of Fig. 1. Such changes are plotted in Fig. 2 for

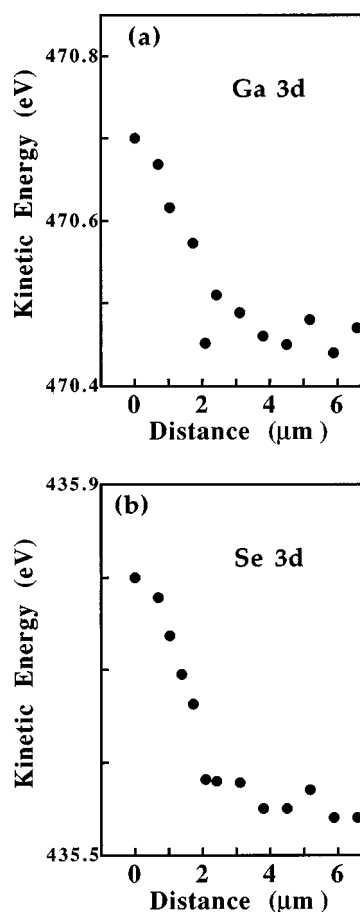


FIG. 2. (a) Kinetic-energy position of the Ga $3d$ peak (taken at 490 eV photon energy) for different positions along the clear dashed line shown in the micrograph of Fig. 1, starting from the Ge-free area. (b) Similar results for the Se $3d$ peak.

both the Ga and Se $3d$ core peaks. Note that the two peaks shift in parallel, which is consistent with a purely electrostatic effect, i.e., with a change in the band bending from place to place.^{3,4} The change occurs over the characteristic distance of the transition from the Ge-free to the Ge-covered area, $\approx 2 \mu\text{m}$; this is approximately twice the estimated Debye length, thus the Debye length does not play a major role in the changes seen in Fig. 2.

The direct evidence for the overlayer-substrate reaction is provided by Ge $3d$ spectra like those of Fig. 3. Even without any detailed line-shape analysis, it is quite clear that the spectra are not consistent with a single $3d$ doublet, and include a second, lower-kinetic-energy component (at a distance of ≈ 1.6 eV with respect to the unreacted-Ge component). It is also clear that the relative intensity of these components increases as one moves from the spots near the Ge-free region (curve B) to those of the Ge-covered region (curve A).

A more detailed least-square-fit line-shape analysis is required to find the other element involved in the reaction. The analysis does not show any evidence of involvement of Ga atoms. On the contrary, the least-square-fit reveals a small but clear reacted component of the Se $3d$ peak, as seen in Fig. 4. The component lies at a kinetic energy 0.2 eV higher than the main GaSe-related Se $3d$ component. Note that the energy shifts of the Ge $3d$ and Se $3d$ reacted components

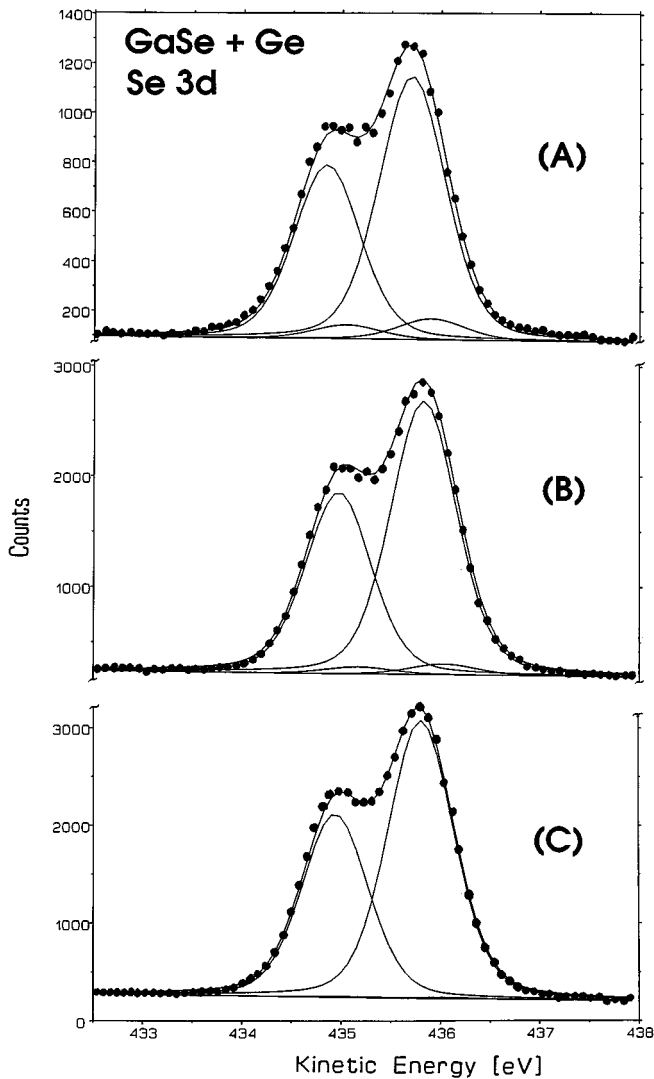


FIG. 3. Ge 3d photoemission spectra taken at 490 eV photon energy on two different microscopic spots along the clear dashed line shown in the micrograph of Fig. 1. Curves A and B were taken at two points 2.9 and 1.0 μm from the origin, i.e., with higher Ge coverage for curve (A) than for curve (B). A Ge-reacted component is clearly visible on the left-hand side of the unreacted component. The results of a two-doublet least-square fit are shown for each spectrum.

match very well those found by Ueno for this kind of reactions.¹³

Further evidence in a favor of Ge-Se chemical interaction is given by the overall trends of the Ge 3d and Se 3d reacted-peak intensities. Figure 5 shows the corresponding plots of the relative intensities of such components as a function of the position along the above-mentioned line. Even with the unavoidable uncertainties for the weak Ge 3d peak, a clear trend is visible, and similar for the two elements.

Preliminary tests were performed to estimate the time scale over which the reaction whose products we detected occurs. These tests indicate a time scale of 5–15 min. As to the driving force for the reaction, we can only offer conjectures. The replacement of Ga-Se bonds with Ge-Se bonds would not appear thermodynamically favorable based on enthalpy consideration, unless perhaps because of the energy

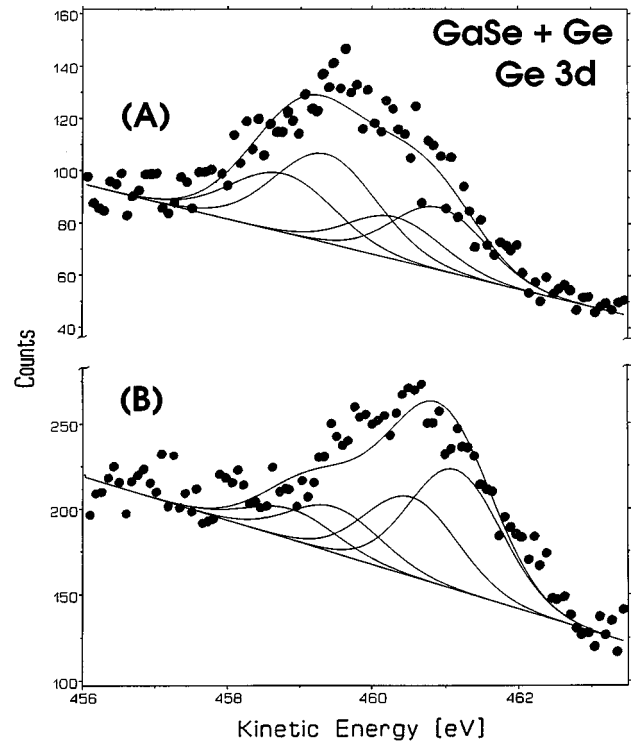


FIG. 4. Results similar to those of Fig. 3 for the Se 3d spectra. Besides the curves (A) and (B) taken at the same spots as curves (A) and (B) in Fig. 3, we show curve (C), which was taken in the Ge-free area, 0.3 μm from the origin. The least-square fit reveals a reacted-Se component for curves (A) and (B), but not for curve (C).

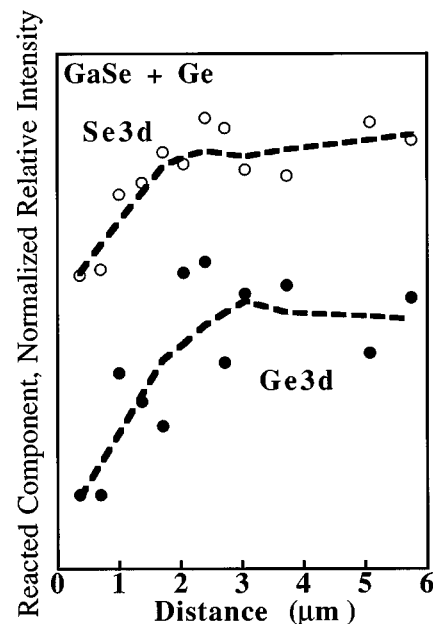


FIG. 5. Relative intensity of the reacted Se 3d and Ge 3d components of spectra similar to those of Figs. 3 and 4, as a function of the position along the clear dashed line in the micrograph of Fig. 1. The dashed lines are least-square weighted fits of the data. The “relative intensity” is defined here as the intensity of the reacted component divided by the total intensity of the spectrum; the data for Se 3d and Ge 3d were normalized so as to have the same average data-point value—in order to emphasize their similar trends.

gained in forming a Ge-Ga eutectic or by some other mechanism related to the low dimensionality of the system.

In conclusion, a local photoelectron-spectromicroscopy analysis on the submicrometer scale clearly revealed evidence of chemical reactions at the GaSe-Ge interface. This is in direct contrast to the commonly accepted notion that this interface is a pure Schottky system—and further decreases the number of interfaces that remain as possible candidates as Schottky systems. As a matter of fact, after eliminating GaSe-Ge no heterojunction interface remains—to the best of our knowledge—as a possible candidate as a pure Schottky system.

Stimulated by these unexpected findings, similar spectro-microscopy tests are currently underway for other interfaces

that are believed to be Schottky systems, notably the interfaces between III-VI semiconductors and unreactive metals. Should these tests once again reveal unexpected chemical interactions, the very notion of “Schottky system”^{3,4} might have to be removed from interface science—even if, paradoxically, this still is the only explanation of metal-semiconductor diodes presented by most of the elementary physics textbooks.

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