

## Microscopic-scale lateral inhomogeneities of the Schottky-barrier-formation process

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The interpretation of photoemission-spectromicroscopy studies of Au on GaSe requires a revision of established ideas about this interface, which has long been considered a prototype of Schottky-like systems. We find that the interface-formation process involves strong substrate-overlayer interactions, the release of free Ga, and the formation of interface species, and leads to a barrier height in total disagreement with the Schottky model. Furthermore, the space-resolving capabilities of our instruments revealed lateral inhomogeneities of the local overlayer thickness and of the local band bending.

### I. INTRODUCTION

We present an application of photoemission spectroscopy to the study of the Schottky-barrier-formation process on a microscopic (micrometer) scale. The interest in moving from conventional, laterally integrated photoemission studies arises, of course, from the possibility of lateral inhomogeneities in the process. And indeed, we discovered an unexpectedly large lateral inhomogeneity for what has been considered for a long time<sup>1-4</sup> a prototype of a very simple Schottky-like<sup>5</sup> system: Au on GaSe.

Two parallel experiments conducted with two different photoemission spectromicroscopes enabled us to show instead that the system is much more complex than it was previously thought: the Schottky barrier is not consistent with the classic Schottky model;<sup>5</sup> the interface formation involves complex substrate-overlayer interactions. Last but not least, we clearly see that different stages of the formation process coexist for the same nominal coverage—giving different values of the band bending from place to place.

The experiments were conducted with the Scienta ESCA 300 electron-imaging photoemission spectromicroscope of the EPFL Centre de Spectromicroscopie in Lausanne,<sup>6</sup> and with the scanning photoemission spectromicroscope MAXIMUM at the Wisconsin Synchrotron Radiation Center.<sup>7</sup> Earlier experiments on *clean* semiconductor surfaces with MAXIMUM had revealed large lateral inhomogeneities in the Fermi-level pinning position, most likely due to changes in band bending.<sup>8,9</sup> This raised the possibility of similar inhomogeneities in the case of interfaces. We considered the GaSe-Au system for the following reasons: This interface had been proposed for several years<sup>1-4</sup> as an almost ideal Schottky system, because of the reported<sup>1</sup> low reactivity of Au on GaSe, a layered compound in the III-VI family. Earlier photoemission experiments<sup>1,2</sup> had produced an *n*-type Schottky-barrier value  $\Phi_n \approx 0.7$  eV, essentially in agree-

ment with the classic Schottky model.<sup>5</sup> They had also suggested little or no chemical interaction between overlayer and substrate. To the best of our knowledge, no experiment had explored in detail the Au-thickness dependence of the interface-formation process. And certainly no experiment had explored its microscopic lateral dependence.

### II. EXPERIMENTS WITH MAXIMUM

The experimental procedure, except for the use of lateral resolution, is consistent with the standard method<sup>10</sup> to study metal-semiconductor interface-formation processes by photoemission spectroscopy of progressively thicker metal overlayers on *in situ* cleaved semiconductor

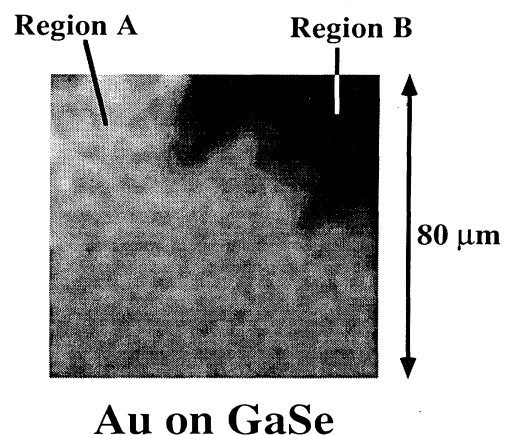


FIG. 1. Scanning photoemission micrograph of a cleaved GaSe surface with a Au overlayer whose nominal thickness was 2 Å, taken at a photon energy of 95 eV, detecting photoelectrons corresponding to the Au 5*d* states. The darker areas correspond to a larger Au photoemission signal.

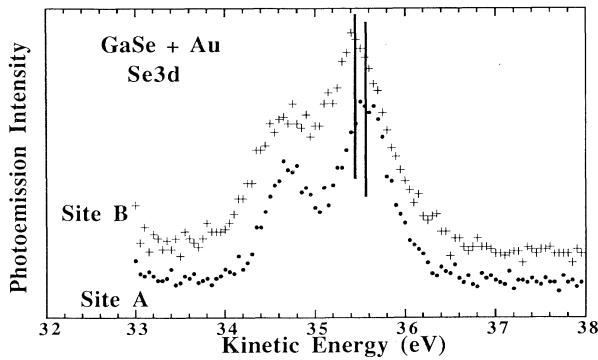


FIG. 2. Se 3*d* photoemission peaks from the two different regions of Fig. 1.

surfaces. The two experimental systems have been described in detail elsewhere.<sup>6,7</sup>

Figures 1–3 show the main point of our study. The image of Fig. 1 is a photoelectron micrograph, obtained with MAXIMUM by focusing a monochromatized 95-eV undulator beam of synchrotron radiation down to sub-micrometer size, and then scanning the sample while detecting the photoemission signal.<sup>7</sup> The filtered photoelectron energy corresponds to the Au 5*d* states of the overlayer, which had a nominal thickness of 2 Å. The difference in the photoelectron signal intensity between the regions *A* and *B* (with *B* being the most intense) clearly reveals inhomogeneities in the Au overlayer thickness.

Such thickness inhomogeneities also correspond to differences in the electronic energies. We see indeed in Figs. 2 and 3 that the GaSe substrate's Se 3*d* and Ga 3*d* photoemission peaks have different kinetic energies in the two regions, with a rigid shift of  $\approx 0.15$  eV towards larger kinetic energies on moving from *B* to *A*.

### III. EXPERIMENTS WITH Al $K\alpha$ RADIATION

In order to clarify the nature of these inhomogeneities, we explored the same formation process in detail as a

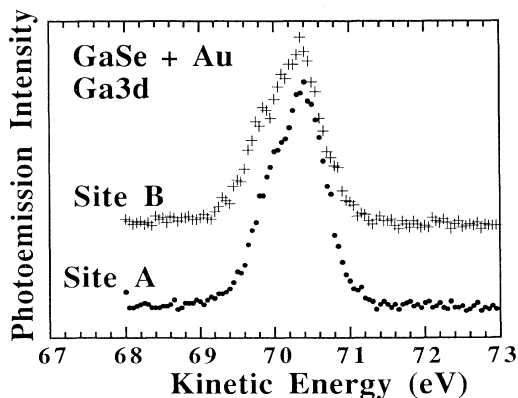


FIG. 3. Data similar to those of Fig. 2, taken for the Ga 3*d* peak.

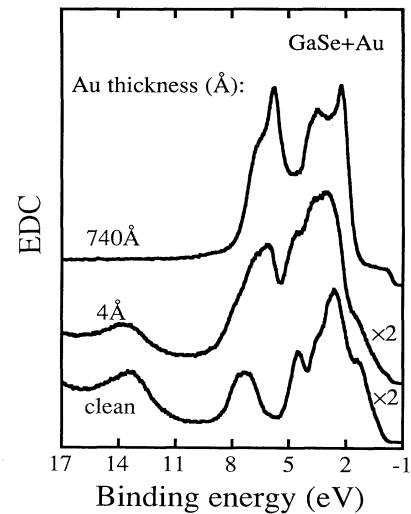


FIG. 4. Valence-band photoemission spectra [energy distribution curves (EDC)] of clean and Au-covered GaSe, taken at a photon energy of 1486.7 eV (Al  $K\alpha$ ).

function of the overlayer thickness with the ESCA 300 photoemission spectromicroscope, using Al  $K\alpha$  radiation. These experiments produced surprising results, in light of the supposed Schottky nature of the system.<sup>1–4</sup>

First of all, we found that there exists a large band bending on the clean cleaved surface of GaSe. This is evident from Figs. 4 and 5, which show the spectral region immediately near the Fermi energy for clean and Au-covered GaSe. Figure 4, in particular, reveals a very large shift, and therefore, a band bending (the GaSe is *p* type, Sn doped,  $p \approx 10^{18}$  cm<sup>-3</sup>).<sup>11</sup> The cause of the band bending has not been identified. We note, however, that

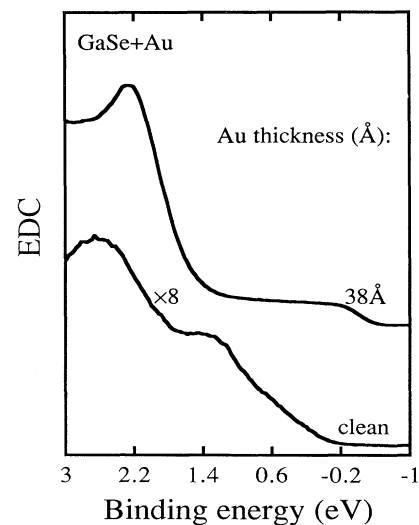


FIG. 5. Direct comparison of the Al  $K\alpha$  photoemission spectra for the top of the clean-GaSe valence band and for the Fermi edge of a thick (38 Å nominal) Au overlayer.

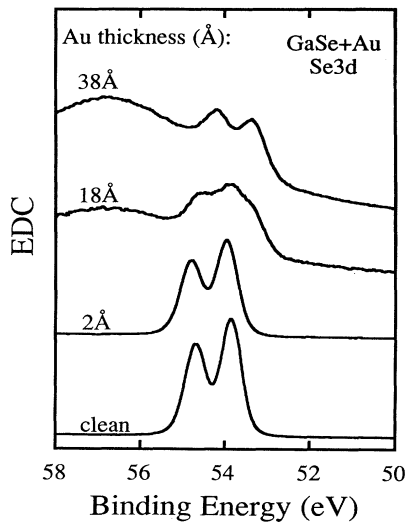


FIG. 6. Al  $K\alpha$  Se  $3d$  photoemission spectra of clean and Au-covered GaSe.

we consistently observed it for GaSe samples obtained with different preparation processes, and it is clearly visible in older data on this material.<sup>3,4</sup> We also note that the observation of such a large and photon-beam-intensity independent band bending indicates that surface photovoltage effects<sup>12</sup> are minimal or nonexistent for this material, probably due to a large recombination rate at room temperature.

The second somewhat unexpected result was the evidence for complex processes during the interface formation, rather than of simple near-physisorption.<sup>1,2</sup> Some evidence for such processes is already present in the Au-covered GaSe data of Fig. 4. The evidence becomes very clear, however, in the Se  $3d$  peaks of Fig. 6. We see at first some small Au-induced energy shifts of this spin-orbit doublet.

At nominal Au coverages of 18 Å, however, the single doublet is replaced by a more complex spectrum. The least-square fit of Fig. 7 reveals indeed two separate dou-

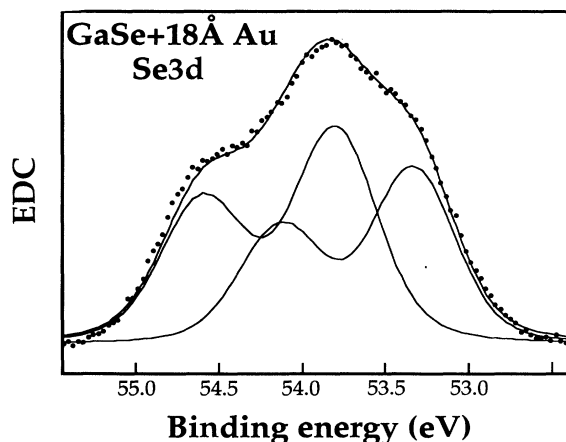


FIG. 7. Best fit of the 18-Å coverage spectrum of Fig. 6.

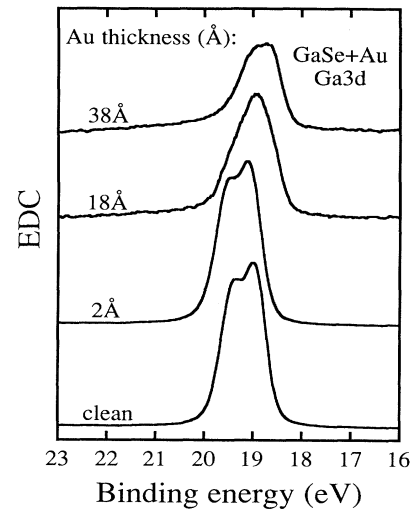


FIG. 8. Al  $K\alpha$  Ga  $3d$  photoemission spectra of clean and Au-covered GaSe.

blets, shifted by  $\approx 0.48$  eV. The left-hand-side doublet corresponds to the two main peaks of the clean-surface and low-coverage spectra of Fig. 6. The right-hand-side doublet of Fig. 7 is instead a new component, which becomes the leading one for the top, largest-coverage spectrum of Fig. 6.

These Se  $3d$  results find their counterpart in the Ga  $3d$  and Au  $4f$  data. In the case of Ga  $3d$ , the spectra of Fig. 8 indicate again a marked change on going from 2 to 18 Å of nominal Au coverage, as for Se  $3d$ . The change is not a mere shift, but a modification of line shape. The least-square fit of Fig. 9 indicates in fact that the main spin-orbit doublet of the clean surface is accompanied by another spectral component shifted to the right, whose

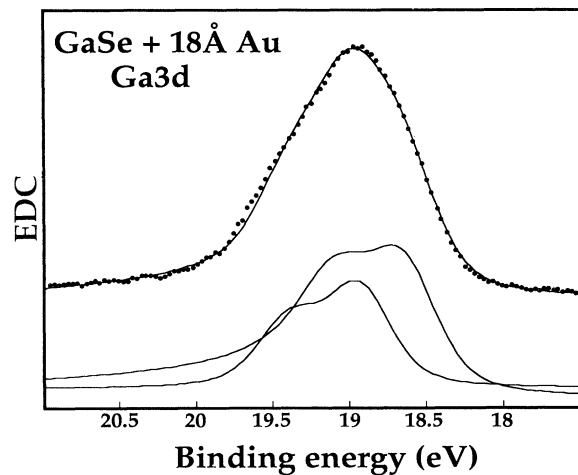


FIG. 9. Best fit of the 18-Å coverage spectrum of Fig. 8. The low-binding-energy doublet exhibits a marked Doniach-Sunjić asymmetry (Ref. 13), reflecting the metallic environment of the corresponding atoms; the asymmetry parameter is 0.2.

intensity increases with the Au coverage as the second Se 3*d* component.

As to Au 4*f*, the spectra of Fig. 10 show a clear change in the energy position at nominal coverages above 4 Å. The shift does not follow a parallel shift of the substrate core levels; therefore, it indicates that the chemical status of Au at low coverage is different with respect to that in the metallic thick-Au overlayer.

As to the nature of the complex process, one possible model is that Au, rather than being nearly physisorbed, interacts heavily with the substrate, disrupting its chemical bonds and promoting the formation of an interface phase. The new Ga 3*d* component is consistent with the presence at the interface of free Ga, released by this bond-breaking process.<sup>1</sup> Note, in particular, its asymmetry, reflecting a metallic environment. The Au and Se core-level data indicate instead the formation of an interface alloy phase. The addition of Au causes both the increase of the metallic Au phase and that of the non-GaSe components, up to fairly high coverages.

The discovery of substantial Au-GaSe interaction is in sharp contrast with the results of Refs. 1 and 2 for Au on *n*-type GaSe, from which no interaction was inferred. Our results are instead reminiscent of those obtained in Ref. 1 for Ni on GaSe, which were interpreted in terms of a strong interaction leading to the release of free Ga.

The complexity of the spectra, reflecting the complexity of the interface-formation process, requires some careful analysis to extract the information on the Schottky-barrier height. In order to follow the band-bending changes with respect to the clean surface, we identified all components of each set of data by best fittings (as in Figs. 7 and 9), then specifically identified those related to the substrate, checking this identification against the requirement of parallel shifts for Ga 3*d* and Se 3*d*.

The results of this analysis are shown in Fig. 11 for a specific set of data taken on a given substrate—and are

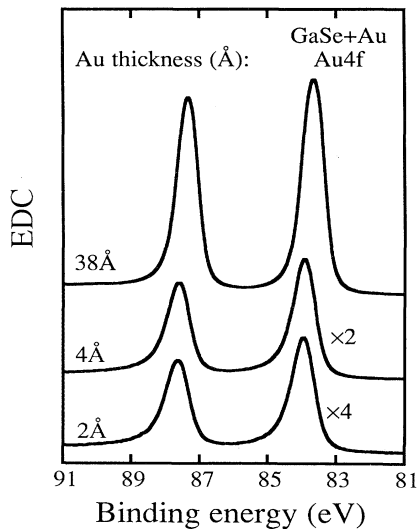


FIG. 10. Al  $K\alpha$  Au 4*f* photoemission spectra of Au-covered GaSe.

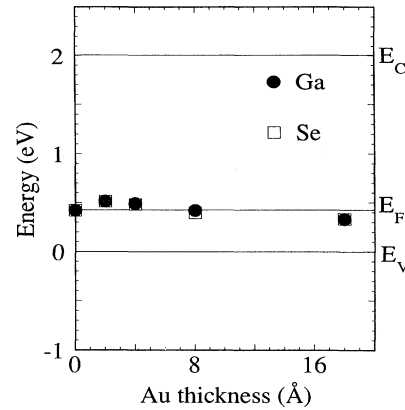


FIG. 11. The Fermi level ( $E_F$ ) position relative to the GaSe valence-band edge, for a Au overlayer on GaSe, as a function of the nominal Au thickness. The final distance between  $E_F$  and the top of the GaSe valence band  $E_v$  corresponds to the *p*-type Schottky-barrier height,  $\approx 0.4$  eV, in total disagreement with the Schottky model (Ref. 5) originally proposed for this class of systems (Refs. 1–4).

consistent with data taken on other substrates. Essentially, we see limited changes in the band bending as the Au coverage increases: a small increase at first, followed by convergence to a value close to the clean-surface one.

Figure 11 indicates, therefore, a *p*-type Schottky-barrier height which is not much different with respect to the distance in energy between the Fermi level  $E_F$  and the surface-interface valence-band-edge position  $E_v$  which is 0.42 eV. Taking into account the experimental uncertainty, we find therefore a *p*-type Schottky-barrier height  $\phi_p \approx 0.4$  eV. This is clearly not consistent with the *n*-type value of 0.7 eV reported in Refs. 1 and 2, since the GaSe gap is 2.05 eV. This also implies that our findings are in sharp contrast with the prediction of the classic Schottky model.<sup>5</sup>

#### IV. CONCLUSIONS

The discrepancies between our data and those of Refs. 1 and 2 do not find an immediate explanation, since the only clear difference between the two experiments is the doping of the substrate. We can safely conclude, however, that Au on GaSe is not, or at least not always, the “ideal” Schottky system that it was thought to be for a long time, but a complex and rather reactive interface.

We further conclude that lateral inhomogeneities exist in the interface-formation process at a given nominal Au coverage. At overlayer thicknesses comparable to those of Figs. 1–3, the Scienta ESCA 300 data reveal a parallel  $\approx 0.1$  shift of the Ga 3*d* and Se 3*d* core level, followed at slightly larger coverages by a countershift of the same magnitude. The data of Figs. 2 and 3 show that the 0.1-eV shift really corresponds to an average over inhomogeneous shifts of smaller and larger magnitude. There appears to be a correlation between the local Au thickness and the local magnitude of the Ga 3*d* and Se 3*d* shifts. Note that the estimated Debye length, of the or-

der of 0.1  $\mu\text{m}$ , is much smaller than the lateral length scale for Figs. 1–3, so observing lateral inhomogeneities related to band bending is possible.

In conclusion, our study of what we expected<sup>1–4</sup> to be a simple and probably homogeneous Schottky-like metal-semiconductor interface-formation process yielded several unexpected results: the system does not behave at all according to the Schottky model,<sup>5</sup> its formation involves a strong substrate-overlayer interaction with disruption of chemical bonds, free-Ga release, formation of one or more interface phases, lateral inhomogeneities concerning the actual local coverage, and band bending at a given nominal Au overlayer thickness, and a *p*-type Schottky barrier in total disagreement with the Schottky-model predictions. We suggest that further experiments with other space-resolved techniques such as

ballistic-electron-emission microscopy could yield interesting results on this system.<sup>14</sup>

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<sup>1</sup>R. H. Williams, A. McKinley, G. J. Hughes, W. Montgomery, and I. T. McGovern, *J. Vac. Sci. Technol.* **21**, 594 (1982).

<sup>2</sup>G. J. Hughes, A. McKinley, R. H. Williams, and I. T. McGovern, *J. Phys. C* **15**, L159 (1982).

<sup>3</sup>R. R. Daniels, G. Margaritondo, C. Quaresima, M. Capozzi, P. Perfetti, and F. Lévy, *Solid State Commun.* **51**, 495 (1984).

<sup>4</sup>R. R. Daniels, G. Margaritondo, P. Perfetti, C. Quaresima, and F. Lévy, *J. Vac. Sci. Technol. A* **3**, 979 (1985).

<sup>5</sup>W. Schottky, *Z. Phys.* **113**, 367 (1939).

<sup>6</sup>G. Margaritondo, C. Coluzza and R. Sanjinés [*Photoemission: From the Past to the Future* (EPFL, Lausanne, 1992)] contains a discussion of this instrument.

<sup>7</sup>A. K. Ray-Chaudhuri, W. Ng, S. Liang, S. Singh, J. T. Welnak, J. P. Wallace, C. Capasso, F. Cerrina, G. Margaritondo, J. H. Underwood, R. Perera, and J. Kortright, *J. Vac. Sci. Technol. A* **11**, 2324 (1993); C. Capasso, A. K. Ray-Chaudhuri, W. Ng, S. Liang, R. K. Cole, J. Wallace, F. Cerrina, G. Margaritondo, J. H. Underwood, J. B. Kortright, and R. C. C. Perera, *ibid.* **9**, 1248 (1991).

<sup>8</sup>F. Cerrina, A. K. Ray-Chaudhuri, W. Ng, S. Liang, S. Singh, J. T. Welnak, J. P. Wallace, C. Capasso, J. H. Underwood, J. B. Kortright, R. C. C. Perera, and G. Margaritondo (unpublished).

<sup>9</sup>Pioneering work in this area has been described in C. Kim, P. L. King, and P. Pianetta, *J. Vac. Sci. Technol. B* **10**, 1944

(1992).

<sup>10</sup>G. Margaritondo, in *Highlights on Spectroscopies of Semiconductors and Insulators*, edited by A. Balzarotti, G. Guizzetti, and A. Stella (World Scientific, Singapore, 1989), p. 387; *Heterojunction Band Discontinuities: Physics and Device Applications*, edited by F. Capasso and G. Margaritondo (North-Holland, Amsterdam, 1987); L. J. Brillson and G. Margaritondo, in *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, Vol. 5 of *Surface Properties of Electronic Materials*, edited by D. A. King and D. P. Woodruff (Elsevier, Amsterdam, 1988), and references therein.

<sup>11</sup>Ph. Schmid, J. P. Voitchovsky, and A. Mercier, *Phys. Status Solidi A* **21**, 443 (1974).

<sup>12</sup>M. Alonso, R. Cimino, and K. Horn, *Phys. Rev. Lett.* **64**, 1947 (1990); M. H. Hecht, *Phys. Rev. B* **41**, 7918 (1990); D. Mao, A. Kahn, G. Le Lay, M. Marsi, Y. Hwu, G. Margaritondo, M. Santos, M. Shayegan, L. T. Florez, and J. P. Harbison, *J. Vac. Sci. Technol. B* **9**, 2083 (1991); D. Mao, A. Kahn, G. Le Lay, M. Marsi, Y. Hwu, and G. Margaritondo, *Appl. Surf. Sci.* **56-58**, 142 (1992), and references therein.

<sup>13</sup>S. Doniach and M. Sunjic, *J. Phys. C* **3**, 285 (1970).

<sup>14</sup>See the discussion in R. Ludeke, A. Taleb-Ibrahim, R. M. Feenstra, and A. D. McLean, *J. Vac. Sci. Technol. B* **7**, 936 (1989), and in W. J. Kaiser, L. D. Bell, M. H. Hecht, and F. J. Grunthaler, *ibid.* **7**, 945 (1989), and references therein.

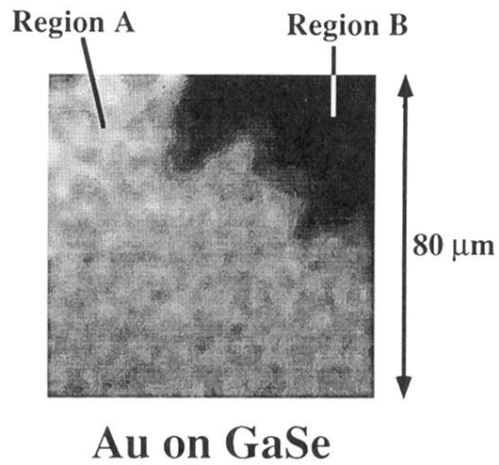


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