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MICROSCOPIC STUDY OF THE SURFACTANT-ASSISTED SI, GE EPITAXIAL GROWTH*

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Abstract

The Sb-assisted Si, Ge epitaxial growth processes have been studied using high resolution photoemission. It is found that the initially ordered Sb monolayer on the Si(100) and Ge(100) surfaces occupies the epitaxial sites and fully saturates the surface dangling bonds. This results in a reduction of the surface energy. During the growth process, the Sb atoms and the deposited Si, Ge atoms change their positions. Sb atoms segregate to the growth front to form a new ordered layer while leaving uniform epitaxial Si, Ge layer behind.

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High quality growth of epitaxial Si, Ge film has attracted much attention recently. The driving force mainly comes from the potential application of SiGe alloy and Si, Ge strain layer structures in new generation semiconductor devices such as high speed devices [1], optoelectronics applications [2]. It is also of fundamental importance to understand epitaxial growth process in general including the interplay among surface, interface free energy and lattice strain relief. For the Si/Ge system, the preferred surface termination is Ge, determined by the free energy difference between the two species. Due to the lattice mismatch between the two, Ge can grow on the Si(100) surface following Stranski-Krastanov mode (layer-by-layer growth for ~3 monolayers that are followed by island formation). In contrast, Si starts islanding from the beginning of the growth on the Ge(100) surface. In order to achieve uniform growth, growth temperature has been pushed lower and lower in various growth techniques. However, the achievement of the overlayer uniformity is based on sacrifice of its crystallinity. Therefore, there is an urgency to look for other strategy. Recently, it has been demonstrated that when the growth front is terminated by a specific third species, the so-called surfactant, which is energetically favored over either Ge or Si termination and always moves with the growth front, Si and Ge growth mode can be dramatically changed. There, three-dimensional (island) growth has been converted into two-dimensional (layer) growth up to a reasonable thickness that is much larger than the "critical thickness", and the uniform epitaxial Si, Ge layer growth can be realized [3]. A number of atoms, such as As, Sb, and Te, have been used as surfactants [3-5].

Although the surfactant-assisted Si and Ge epitaxial growth process is under active investigation, the growth mechanism is not well understood yet. The goal of this work is to provide a microscopic description of such a growth process at the atomic scale. High resolution photoelectron spectroscopy has been used in this work. Here, we carefully study the growth process at various stages, paying special attention on the structural and

electronic properties, particularly the role of surfactant during the entire growth process. Sb was used as a prototypic surfactant to examine such a growth process because Sb/Si(100) and Sb/Ge(100) have long been viewed as model systems and studied rather intensively. Also, Sb is relatively easier to handle with precise control compared with As, so that a quantitative study is feasible. We found that the ordered Sb layer occupies the epitaxial sites and saturates the surface dangling bonds of both Si(100) and Ge(100) surfaces, and thus reduces the surface energies. During the growth, Sb and incoming species exchange their positions. As a result, Sb moves to the growth front to form new ordered layer, while leaving epitaxially grown film behind.

The experiment was carried out at the Stanford Synchrotron Radiation Laboratory on beam line I-2 with a 6-m toroidal grating monochromator. A ultrahigh vacuum VG ADES400 angle-resolved system equipped with a hemispherical analyzer was used with combined resolution about 0.25 eV. The Si and Ge wafers were cut along (100) orientation with less than 1° miscut. The Si(100) samples were chemically cleaned and etched in 48% HF solution for a fraction of a minute before introduced into the system. The samples were then prebaked at ~500°C for about an hour and annealed to ~900°C to drive away hydrogen. The Ge(100) samples were cleaned by thermal annealing at ~800°C. Sharp two-domain (2x1) diffraction patterns were observed from the low energy electron diffraction (LEED) optics on these surfaces. Sb and Ge were evaporated from tungsten filament evaporators, and Si was evaporated with an electron beam evaporator. Thorough outgassing was performed prior to deposition. The pressure was kept in 10^{-10} torr range during sample cleaning and evaporation with a base pressure around 1×10^{-10} torr. No trace of contamination was found within the sensitivity of photoemission.

The Si, Ge heteroepitaxial growth process is as the following: after the Si(100) [Ge(100)] surfaces were thermally cleaned, a couple of monolayers of Sb were deposited on the

surfaces at room temperature. The interfaces were then annealed to ~500°C. As will be seen later, such a treatment leads to formation of an ordered Sb monolayer residing on the top surfaces. Ge (Si) was then deposited on to the structures at room temperature followed by thermal annealing at ~500°C or at elevated temperature (~500°C). The observed LEED pattern and angle resolved valence band photoemission spectra indicate that the growth structures are well ordered and occupy the epitaxial sites.

Let us first examine the substrates at various stages during the epitaxial growth process. Figure 1 shows the substrate Si 2p and Ge 3d spectra, together with the decomposed components using least square fitting. The spectra have been moved to correct the band bendings of the substrate. The spectra of the clean surfaces exhibit obvious shoulders (S) on the low binding energy side relative to the main (B) peaks. They have been identified as the surface core-level shifts, and it is generally agreed that they are associated with the dangling bonds from the top surface atoms [6,7]. When several monolayers of Sb were deposited on these surfaces at room temperature followed by thermal annealing around 500°C, only one monolayer of Sb remains on the surfaces [8]. A (2x1) LEED pattern with weak, diffuse half-order dots was observed. The Sb/Si(100) interface has been studied by Norgami *et al* using scanning tunneling microscope (STM) [9]. They showed that Sb atoms formed dimers rows that were perpendicular to the original Si dimer rows, and the original Si dimers were then relaxed. It is important to notice that the Sb atoms reside exactly where the Si atoms should be located in the case of Si homoepitaxial growth. The weak and diffuse half-order dots in the LEED pattern results from break of the Sb dimer rows. Similar behavior with somewhat better ordering has also been reported at the As/Si(100) interface [10,11]. Influence of the Sb overlayer over the electronic properties is reflected by the removal of the surface related core level shift from the clean surface spectrum, as shown in fig. 1(a). Our results are in agreement with the previous study [12]. This provides a strong evidence that the Si(100) surface dangling bonds are saturated, and

as a result the surface energy is reduced. The behavior of Sb on the Ge(100) surface is nearly identical to that of the Sb/Si(100), which is evidenced by observation of identical LEED patterns as well as analogous dispersive behavior in the angle resolved valence band spectra. As with the Si(100), Sb saturates the Ge(100) surface dangling bonds as shown by the spectrum shown in Fig. 1 (b).

Next, the behavior of the surfactant and the grown material will be examined. For sake of brevity, we are going to concentrate on the Ge epitaxial growth on the Si(100) surface. The conclusions can be directly applied to the Si epitaxial growth on the Ge(100) case. Figure 2 shows the Sb 4d and Ge 3d spectra at various stages of Ge epitaxial growth on the Si(100) surfaces. Strong emission from the Sb 4d is observed when a couple of monolayers of Sb were deposited on the Si(100) surface at room temperature. After mild annealing, the intensity decreases. The remaining Sb on the surface is estimated to be about one monolayer. Notice that the Sb 4d spectrum now only consists of one doublet component. This essentially indicates occupation of a single type of Sb site on the Si(100) surface, in accordance with the fact that Sb forms ordered layer.

When Ge is deposited on this structure at room temperature, several changes take place. The first obvious change is strong reduction of the Sb 4d peak intensity. The degree of this intensity decrease is indicative of the uniform Ge overlayer on top of the Sb layer. In addition to the intensity decrease, Sb 4d becomes much broader compared with that without Ge overlayers. The Ge 3d spectrum is also broader with unresolved spin-orbit splitting features. These spectra changes suggest that the deposited Ge is a disordered state. Lack of crystallinity in the deposited Ge layer is corroborated by disappearance of LEED pattern in this case. The situation is, however, completely different when this structure undergoes a thermal annealing at around 500°C. First, there is a recovery of the intensity of the Sb 4d spectrum and loss of the Ge 3d intensity. In fact, the intensity of the Sb 4d in this case is

the same as that on the Sb/Si(100) surface. No depletion of Sb has been detected. This clearly demonstrates that Sb layer now resides on the top surface. Second, the Ge 3d spectrum is much more defined. The filled valley in curve c reappears, indicating much improved crystallinity in Ge layer. In fact, this spectrum is nearly identical to that shown in figure 1, when the single crystal Ge(100) surface is covered by an ordered Sb layer. Finally, a LEED pattern [(2x1) with weak, diffuse half-order dots] is seen again.

From this set of spectra, we can easily draw several conclusions. It is clear that during the annealing, Sb atoms and Ge atoms exchange their positions. As a result, Ge atoms move in and make direct contact with the Si substrate, while Sb atoms move out to the top surface, a typical behavior of a surfactant. Energy minimization calculations show that it is energetically favorable to form As/Si/Ge over Si/As/Ge, a driving force for As segregation to the top surface [3]. It appears that such a relationship is likely to hold when As is replaced by Sb. Moreover, Ge atoms are no longer arranged in a random fashion. Instead, they appear to occupy the epitaxial sites of the substrate Si(100), which is evidenced by the reappearance of the LEED pattern as well as the well resolved Ge 3d spectrum. Meanwhile, the segregated Sb atoms also form an ordered layer on the growth front. It should be pointed out that the mobility of the incoming species is strongly curtailed, and thus minimizes the tendency of cluster formation during the growth. In most conventional growth methods, high surface mobility at high temperature may result in nonuniform growth, while reduced temperature limits the ability for the incoming atoms to search for the epitaxial sites. With the assistance from the surfactants, one is able to grow more uniform epitaxial layers at relatively low temperature, mainly because the epitaxial sites are available, provided by the outgoing surfactants. Therefore, the incoming atoms don't have to travel a long distance to find such sites.

Further evidence supporting the formation of the epitaxial Ge layer on the Si substrate comes from the narrowing of the substrate Si 2p core level spectrum of the Sb/Ge/Si(100) structure shown in fig. 1 (a). This is manifested by the increased intensity ratio between the Si $2p_{3/2}$ and the valley. This clearly indicates that the Si 2p is closer to its bulk lineshape, implying that the substrate is in a bulk-like environment. Careful data analysis reveals that an extra surface related component S', which still exists at the Sb/Si(100) interface and is identified as the contribution from the subsurface of the Si(100) clean surface, is eliminated from the spectrum of the Sb/Ge/Si(100) structure [7]. Essentially, it is because a few epitaxial Ge layer, which have electronic and chemical properties similar to those of Si, fully relax the substrate, resulting in removal of all the non-bulk component originating from top few layers of the Si(100).

Segregation and ordered layer formation of Sb during thermal annealing end one growth cycle and make the whole system ready for further epitaxial growth. In fact, We repeated the same procedure for several times and obtained thick Ge epitaxial film on the Si substrate. The epitaxial Ge film can also be obtained by direct depositing Ge on Sb/Si(100) structure at elevated temperature, which was used previously by other groups [3-5]. The same method has been applied in epitaxial Si growth on the Ge(100) substrate. Uniform epitaxial layer could be grown, in sharp contrast to the non-uniform growth without surfactant [13].

The electronic properties of the grown epitaxial structures have been studied using angle-resolved photoemission. They are illustrated by the sets of angle resolved valence band spectra presented in figure 3. The strong dispersion observed in these valence band spectra once again demonstrates that all the structures shown in this figure have high degree of orderness. A detailed discussion of valence band structure as well as valence band discontinuity will be discussed elsewhere [14].

In summary, we have demonstrate that an ordered surfactant layer on the Si(100) and Ge(100) surfaces occupies the epitaxial sites and saturates the surface dangling bonds. As a result, the surface energy is reduced, providing a base for uniform growth. During the growth process, surfactant atoms and the deposited Si (Ge) atoms exchange their positions. Si (Ge) atoms move in and take the epitaxial sites vacated by the outgoing surfactant atoms and make direct contact with the substrate. Consequently, surfactant atoms move to the growth front and form a new ordered overlayer, leaving a uniform epitaxial layer behind. The whole system is then ready for further growth. This work was performed at SSRL, which is supported by Department of Energy, Office of Basic Energy Science, Division of Chemical Sciences. The authors would also like to acknowledge the support of that Office's Division of Material Science for this research.

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Figure Captions

Figure 1. Si 2p and Ge 3d core level spectra of the surfaces during Sb-assisted Si, Ge heteroepitaxial growth: (a) Ge growth on Si(100) surface; (b) Si growth on Ge(100) surface. All the spectra have been decomposed using computer least square fitting and the fitting parameters and procedure can be found in Ref 7.

Figure 2. Sb 4d and Ge 3d core level spectra at different stage of Ge epitaxial growth on the Si(100) surface with Sb as a surfactant. (a) a couple of Sb monolayers deposited on the Si(100) surface at room temperature; (b) after ~500°C annealing of structure (a), resulting in one ordered Sb overlayer; (c) Ge deposition on the 1ML Sb/Si(100) structure at room temperature; and (d) ~500°C annealing of structure (c).

Figure 3. Angle resolved valence band spectra taken at a photon energy of 21 eV as a function of emission angle along [100] direction (incident angle is 45°).

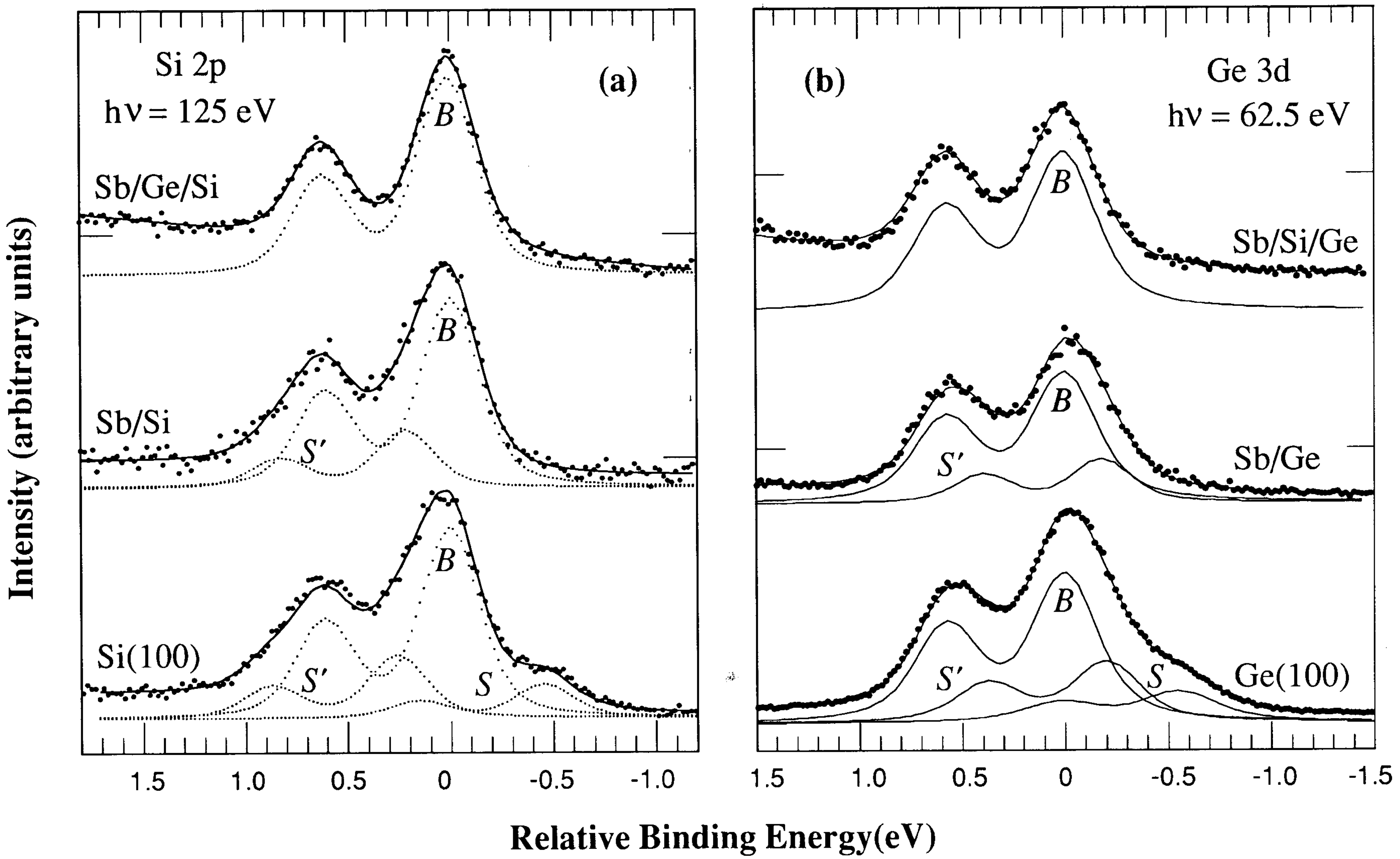

Fig. 1

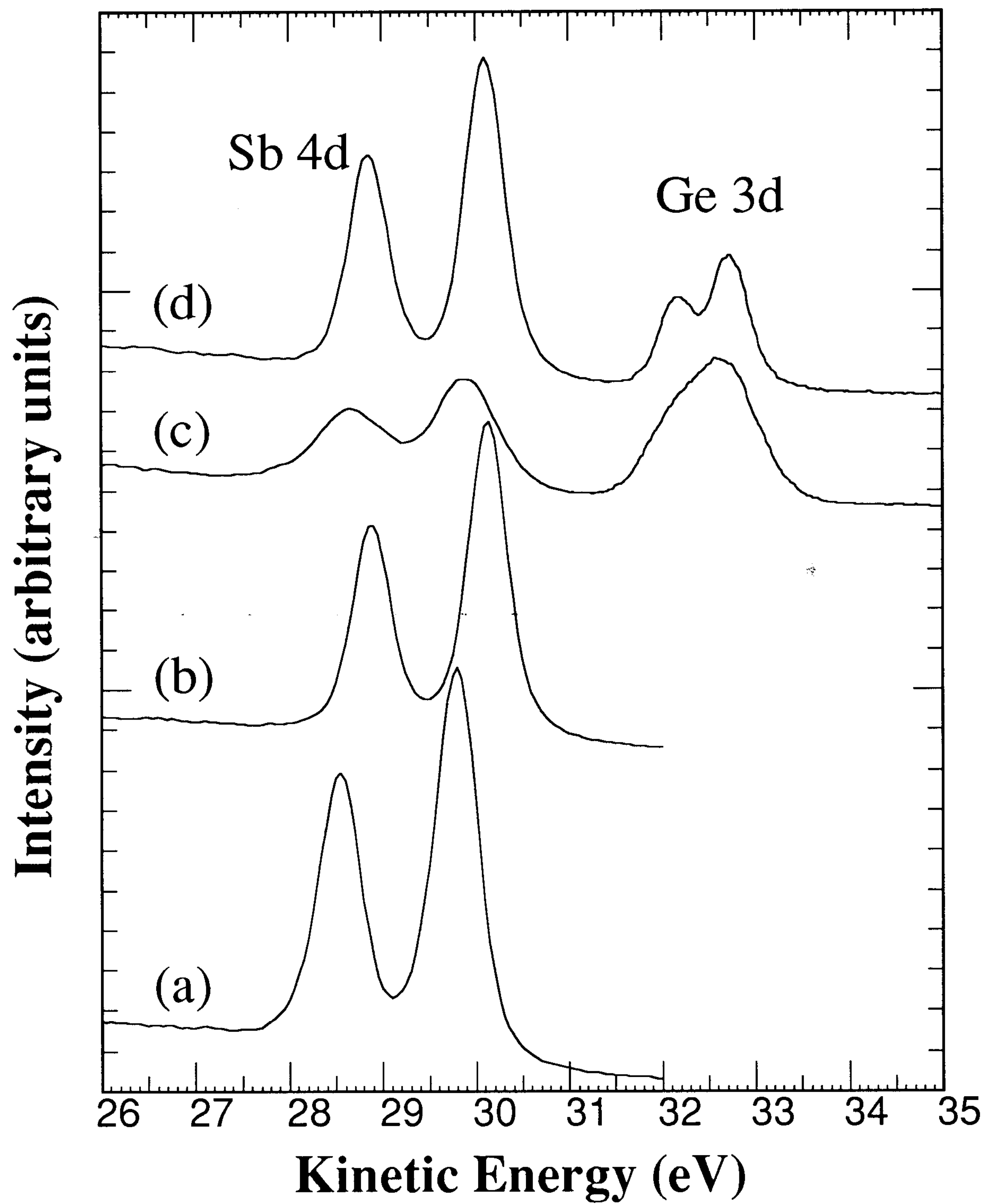

Fig. 2

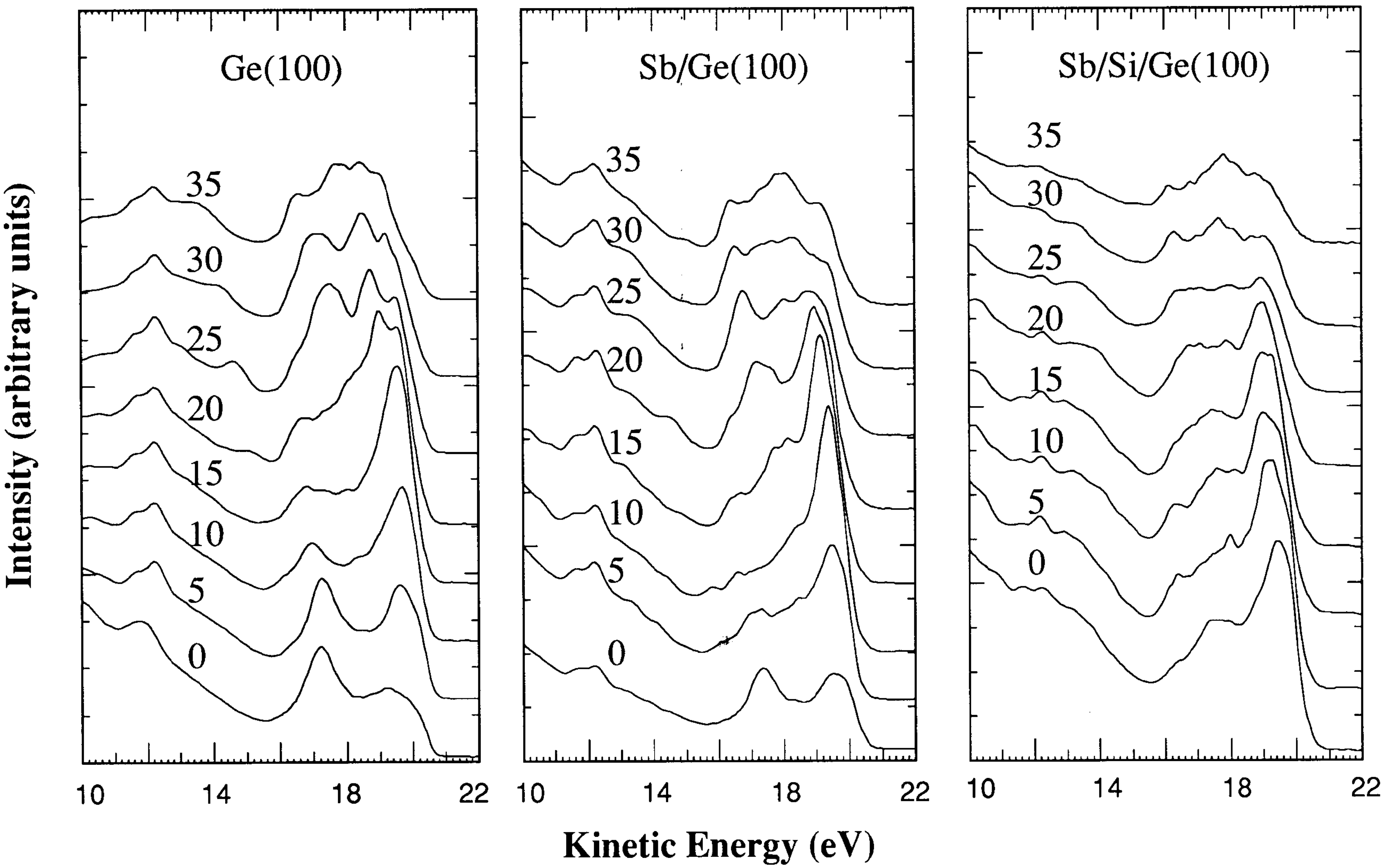

Fig. 3