

Intermixing at Pb/Ge(111) and Pb/Ge(001) interfaces studied with electron-energy-loss spectroscopy

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In the present work, the interfacial reactions of the Pb/Ge(111) and Pb/Ge(001) systems are studied with electron-energy-loss spectroscopy, low-energy electron diffraction, and Auger electron spectroscopy. In contradiction to previously obtained results, we find that Pb intermixes strongly with Ge at the interfaces of both systems, forming a special intermixed interfacial phase, which is in every sense very similar to the intermixed interfacial phase reported very recently as existing at the interfaces of the Pb/Si(111) and Pb/Si(001) systems. Oxygen contamination may suppress the Pb-Ge intermixing completely. The same situation arises in Pb/Si systems.

Despite the fact that the formation mechanism of the Schottky barrier (SB) at metal-semiconductor (MS) interfaces is still an unsettled issue, it is very likely that the local specifics of the interfaces determine the SB height.¹ Obviously, unreactive or abrupt interfaces are easier to tackle in this regard. For this reason, much attention has been paid to the Pb/Si (Refs. 2–12) and Pb/Ge (Refs. 13–22) systems. In a recent article⁴ Le Lay, Hricovini, and Bonnet wrote, “An overview of the recent literature has shown us that Pb constitutes a prototype metal overlayer on several quite different semiconductor substrates. The interface formed appears totally unreactive and extremely sharp.” Very recently, it has been pointed out that both the Pb/Si (111) and Pb/Si (001) interfaces are not abrupt and strong intermixing does exist at both interfaces, resulting in formation of a specific intermixed interfacial phase.¹¹

In the present paper, we have studied the Pb/Ge (111) and Pb/Ge (001) interfaces with electron-energy-loss spectroscopy (EELS), low-energy electron diffraction (LEED), and Auger electron spectroscopy (AES) and have found an intermixed interfacial phase which is very similar to the one existing at the Pb/Si interfaces.¹¹

The experiments were performed in an ultrahigh-vacuum UHV system which was reported before.^{11–13} Briefly, the UHV system consisted of a sample preparation chamber and a main chamber equipped with LEED, EELS, and AES. Lead deposition was carried out in the sample preparation chamber and the pressure was maintained at $(2-6) \times 10^{-10}$ torr while the Pb source was on. The samples with a size of $7 \times 7 \times 0.5$ mm³ were cut from the Sb-doped Ge(111) or Ge(001) wafers (18–20 Ω cm). After Ar⁺ bombardment (5×10^{-5} torr \times 600 V \times 1.5 h) and annealing (800 °C \times 15 min) a clean and well-ordered surface of Ge(111)c(2 \times 8) or Ge(001)2 \times 1 was always obtained as verified by their sharp LEED pattern and the very small AES signals of O and N, i.e., the O(503 eV)/Ge(47 eV) and N(379 eV)/Ge(47 eV) peak-to-peak ratios being below 3×10^{-4} . The construction of the Pb source, the calibration of its deposition rate, as well as the way of annealing, and temperature measurement were

the same as those used in the previous works.^{11–13}

Gradual deposition of Pb with a rate of about 0.1 monolayer/min [1 monolayer (ML) = 6.2×10^{14} atoms/cm² for Ge(001) and 7.2×10^{14} atoms/cm² for Ge(111)] onto the clean Ge(001)2 \times 1 surface kept below 100 °C resulted in the AES intensity curve shown in Fig. 1. The AES intensity of Pb (MOO, 94 eV, peak to peak) increases linearly with Pb deposition till the break point at about 2 monolayers, which marks the appearance of Pb islands. Note that this is significantly different from the conclusion (1 ML) of Le Lay and co-workers.^{4,14,15} Gradual deposition of Pb onto the clean Ge(111)c(2 \times 8) surface resulted in an AES intensity curve that is very similar to the one in Fig. 1, thus not shown. It is interesting to point out that for both the Pb/Si (111) and Pb/Si (001) systems the break point on the AES curve also appears almost at 2 ML of Pb.¹¹

Shown in Fig. 2 is a set of typical EELS curves collected with different primary beam energies from the Ge(111)($\sqrt{3} \times \sqrt{3}$) _{β} -Pb surface.¹⁶ It has been reported that both the Pb/Ge (001) system¹³ and the Pb/Ge (111) system¹⁶ may have many different superstructures appearing at different Pb coverages and/or after different heat treatments. However, the EELS curves collected from the 3 \times 6 and 4 \times 1 superstructures of the Pb/Ge (001) system¹³ as well as the 1 \times 1 and ($\sqrt{3} \times \sqrt{3}$) _{β} super-

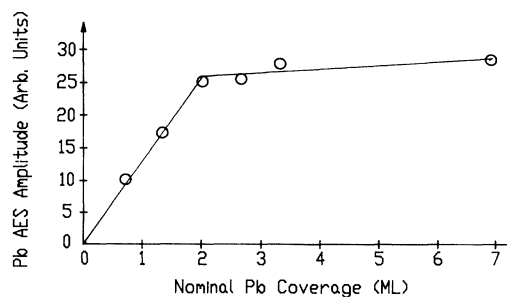


FIG. 1. Evolution of the AES intensity of Pb (MOO, 94 eV, peak-to-peak) in the course of Pb deposition onto the clean Ge(001)2 \times 1 surface kept at the room temperature.

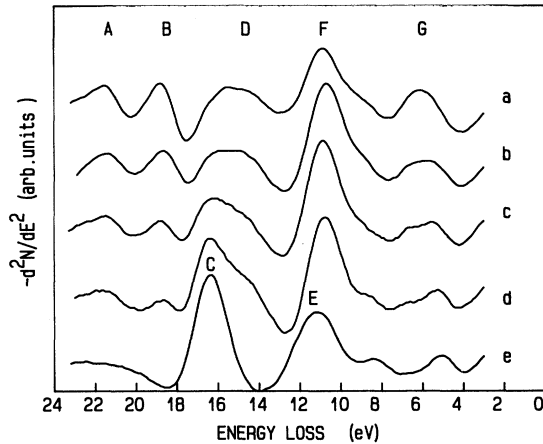


FIG. 2. Electron-energy-loss spectra (a)–(d) measured with different beam energies from the as-deposited Ge(111)($\sqrt{3} \times \sqrt{3}$) $_P$ -Pb surface and a spectrum (e) from the clean Ge(111)c(2 \times 8) surface. The beam energies are (a) 200 eV, (b) 500 eV, (c) 1000 eV, (d) 1950 eV, and (e) 1950 eV.

structures of the Pb/Ge (111) system¹⁶ are actually the same as those in Fig. 2. To give a flavor of the similarities, a comparison is given in Fig. 3. The comparison suggests that Fig. 2 is actually common to these surfaces which belong to different substrate orientations, have different Pb coverages and structures, and have experienced different heat treatments. It is also very interesting to note that the curves shown in Fig. 2 are almost identical with their counterpart collected from the Pb/Si systems.¹¹ We are to discuss the meaning of the above two facts later on. Before that we give another set of EELS curves in Fig. 4, which is expected to facilitate the assignments of the peaks on the curves because on its top and at its bottom the curves from the clean Pb sample^{11,23} and clean Ge surface are shown, respectively, together with the curves from the Pb/Ge system. From previous papers²⁴ we know the origin of the peaks on the EELS

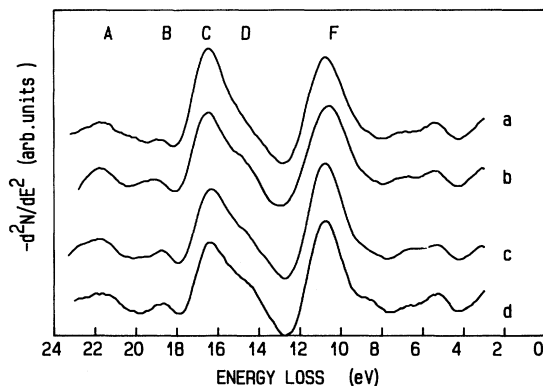


FIG. 3. Electron-energy-loss spectra collected with a beam energy of 1950 eV from the (a) Ge(001)3 \times 6-Pb, (b) Ge(001)4 \times 1-Pb, (c) Ge(111)1 \times 1-Pb, and (d) Ge(111)($\sqrt{3} \times \sqrt{3}$) $_P$ -Pb surfaces, showing the high similarities among the spectra.

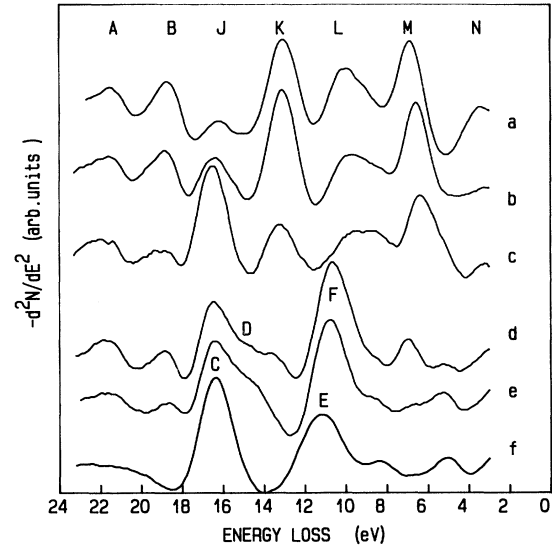


FIG. 4. Electron-energy-loss spectra collected with a beam energy of 1950 eV from (a) the pure Pb sample, (b) the sample prepared by depositing 4 ML of Pb onto the oxygen-contaminated Ge(111) substrate (see text), (c) with 2 ML of Pb [otherwise the same sample as in (b)], (d) the clean Ge(111)c(2 \times 8) with 6 ML of Pb deposited on it, (e) same as (d) but with 2 ML of Pb, and (f) the clean Ge(111)c(2 \times 8) surface.

curve of the clean Pb sample; *A* and *B* are the $5d_{3/2}$ and $5d_{5/2}$ core-level peaks, respectively; *J*, *M*, and *N* are the interband transition peaks, or, more concretely, *M* is from the $6s$ and *N* from the $6p$ band; while *K* and *L* are the bulk and surface plasmon peaks, respectively. As for the EELS curve of the clean Ge(111) surface, it is well known that *C* and *E* are the bulk and surface plasmon peaks, respectively.²⁵

Now, we are ready to understand what happens at the Pb/Ge interfaces through studying the EELS curves shown here. Since the EELS and AES results are so similar for the Pb/Ge and Pb/Si systems, as mentioned above, and the latter has been understood via a quite lengthy reasoning process,¹¹ the results of the former are briefly discussed here.

Compared with the Pb and Ge curves [(a) and (f) in Fig. 4], the Pb/Ge curves [(a)–(d) in Fig. 2 and (d) in Fig. 4] have neither the bulk lead peaks *J*, *K*, *L*, *M*, and *N* nor the germanium surface plasmon peak *E*, but three new peaks (*F*, *G*, and *D*). Obviously, they originate neither from pure germanium nor from pure lead. In view of the energy dependence of the relative peak height shown in Fig. 2, peak *G*, seen mainly on the curves collected with the lower beam energies, ought to originate from the surface, while *F* from a bulk, a different bulk consisting of both germanium and lead atoms. We may call the bulk an intermixed interfacial phase as we did in the case of the Pb/Si system.¹¹ Of course, *F* still could be either the bulk plasmon peak or an interband transition peak of the phase. Considering the fact that its counterpart in the Pb/Si systems is the bulk plasmon peak of the

intermixed interfacial phase,¹¹ F ought to be the bulk plasmon peak of the Pb/Ge interfacial phase. If this is true, then the energy of the corresponding surface plasmon should be around 7 eV, i.e., about $1/\sqrt{2}$ of that of the bulk plasmon. Actually, G has nearly that value and it is indeed a surface peak as we just mentioned. Moreover, there should be an interface between the interfacial phase and the underlying germanium substrate and, according to the dielectric continuum model,^{26–28} the plasmon energy of this interface can be deduced from the energies of the two relevant bulk plasmons, i.e., 16.3 and 10.8 eV, to be about 14.6 eV. In fact, decomposition of the EELS curve shows that D is exactly at this energy position. Taking all these into account, we must say that it is reasonable to assign F and G to the bulk and surface plasmon of the interfacial phase, respectively, and assign D to the plasmon of the interface between the interfacial phase and the germanium substrate.

As the full width at half maximum of peak F (2.3 eV, as determined with decomposition) is equal to that of C (2.3 eV), the interfacial phase must have a quite homogeneous and stable density of free charge as well as atomic structure. This justifies the correctness of calling it a phase.

Comparing curve (d) in Fig. 4 with (e), we see that the relative peak height of peaks F and C maintains the same [although on curve (d) peaks M and K start to emerge, showing the growth of Pb islands on the surface]. This suggests that the interfacial phase reaches its maximum thickness at a Pb coverage of 2 ML, which coincides with the break point of the AES intensity curve shown in Fig. 1 and explains the meaning of the break point. The thickness is estimated¹¹ to be near 10 Å.

Although the interfacial phase must be quite homogeneous, from Fig. 2 we see that the upper layers of the Pb/Ge interfaces must be Pb rich, as justified by the higher relative peak height of A and B to F for lower beam energies. If we assume that 1 ML of the deposited Pb stays on top of the surface and the rest in the interfacial phase, then, according to its thickness, the Pb:Ge

atomic ratio of the phase cannot be larger than 1:4. Nevertheless, Pb must be the minority in the interfacial phase.

It has been known that oxygen contamination can completely suppress the intermixing at the Pb/Si interfaces.¹¹ In the present work we have also studied the influence of oxygen contamination on the interfacial reactions. We contaminated the substrate prior to Pb deposition in the same way as in Ref. 11, and estimated the oxygen coverage according to Ludeke and Koma.²⁵ It turned out that 1–2 ML of oxygen can completely suppress formation of the interfacial phase, resulting in the completely different EELS curves such as (b) and (c) in Fig. 4, which are simply the linear combinations of curves (a) and (f).

Because Pb intermixes strongly with Ge at their interfaces and a small amount of an impurity, such as oxygen, may have dramatic influence on the interfacial reaction and thus on the interfacial structure, it is expected that real interfaces of the Pb/Ge systems may vary markedly from one to another. This might explain the contradiction between this work and previous ones.^{14,15}

In summary, Pb deposited with a rate of about 0.1 ML/min onto the clean Ge(111) $c(2\times 8)$ or Ge(001) 2×1 surface reacts strongly with the substrates even at room temperature, resulting in the formation of a specific intermixed interfacial phase. Regardless of the substrate orientation, heat treatment, as well as the concrete surface structure, the interfacial phase has the following characteristics: (i) Its maximum thickness is about 10 Å, (ii) it has a specific Pb:Ge atomic ratio and Pb is the minority in it, and (iii) its bulk plasmon energy is 10.8 eV.

At the oxygen-contaminated (1–2 ML) Pb/Ge interfaces, intermixing is somehow completely suppressed, as no such intermixed interfacial phase could be found.

All these features are very similar to those happening in the Pb/Si(111) and Pb/Si(001) systems.

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