Phase transitions on the surfaces of germanium and silicon

B. Z. Ol'shanetskiĭ, S. M. Repinskiĭ, and A. A. Shklyaev

Institute of Semiconductor Physics, Siberian Division, USSR Academy of Sciences
(Submitted January 17, 1977)
Pis'ma Zh. Eksp. Teor. Fiz. **25**, No. 4, 195–197 (20 February 1977)

First-order phase transitions of the order-order type take place on clean germanium and silicon surfaces.

PACS numbers: 61.14.Hg, 68.20.+t

It is known that pure surfaces of germanium and silicon crystals, which have the diamond lattice, are restructured and the disposition of the atoms on the surface is characterized by structures that differ from volume planes parallel to the surface, or by superstructures.[1] It was demonstrated earlier by the slow-electron diffraction (SED) method that the superstructures on the surfaces (100) of germanium and silicon—Ge(100)—4×2 and Si(100)—2×1—are stable in a wide range of temperatures.[2] Reversible transitions are observed in the superstructures on clean (111) surfaces of germanium and silicon, as indicated by the changes in the SED patterns.[3–6] A jumplike deterioration of the long-range order takes place in the superstructures on the (111) surface of germanium at 300 °C, and beyond 550 °C no traces of reflections from the superstructure remain on the SED patterns.[6] The corresponding transition in the superstructure Si(111)—7×7 on the surface of silicon takes place near 880 °C.[2,3,5] We report here first-order phase transitions due to jumplike changes of the structure at definite temperatures, which we have observed with the aid of SED on the surfaces of single-component crystals, such as germanium and silicon. These transitions were observed by us on clean (110) germanium and silicon surfaces. By now we have obtained experimental proof of the presence of such transitions also on certain vicinal surfaces of germanium. These transitions take place in the following manner.

The (110) surfaces of germanium possess at room temperature a superstructure Ge(110)—8×10. When the sample is heated, this surface turns at 380°C into an aggregate of facets whose planes are rotated 4°20′ relative to the (110) planes. The facet dimensions amount to several hundred angstroms. The indices of the planes of the facets are (17, 15, 1), (17, 15, $\bar{1}$), (15 17 1), and (15 17 $\bar{1}$). Such a surface is stable up to 430 °C, when a new realignment takes place, into a flat surface with superstructure Ge(110)—8×10. The change from the high-temperature to the low-temperature structure requires several dozen minutes. If facet planes are produced on the surface of a sample and the sample is rapidly cooled, no time is left for the restructuring and the high-temperature surface crystalline phase remains quenched.

It is known that a number of superstructures are observed on a clean surface of silicon,[7,8] but no unambiguous correspondence has been established so far between the heat treatment of the sample and the observed superstructures. We have noted that a number of crystalline surface phases are possible on the (110) surface of silicon. The surface has a superstructure Si(100)—4×5 at

temperatures below 600 °C, Si(100)—2×1 above 600 °C, with a restructuring into Si(110)—5×1 at a temperature close to 650 °C. These transitions are fully reversible. The transition from Si(110)—5×1 to Si(110)—2×1 is stretched out approximately 30° below 750 °C and proceeds via the intermediate structures Si(110)—7×1 and Si(110)—9×1. We were unable to determine exactly the temperatures of the transitions between these intermediate structures. The reason why each of these structures can sometimes be observed also at room temperature is that in this case the change of the high-temperature structure into the low-temperature structure calls for a time of one or two minutes, which may exceed the cooling time of the sample. The hitherto investigated high-index surfaces of various crystals oriented at angles 5—15° to the low-index faces turned out to be faceted by low-index planes interconnected by steps that were usually one atom high. This led to the conclusion[9] that such a structure is a property inherent in all high-index surfaces, regardless of the type of the chemical bond in the crystal. The results of our investigations of surfaces at small angles to the (100) and (111) planes of germanium agree with this statement. However, in the investigation of surfaces at small angles to the (110) planes, it turned out that for surfaces that are rotated about the directions $[1\bar{1}0]$ and [001], which coincide with the directions of the atomic rows on the (110) surface, the equilibrium surface at room temperature is the one made up of facet planes. These are the planes (17 15 1) and (15 17 1) in the former case and (10 9 2) and (10 9 $\bar{2}$) in the latter. We investigated germanium surfaces rotated 3°30′ around the $[1\bar{1}0]$ direction and 6°40′ and 13°20′ around the [001] direction. At high temperatures, these surfaces become steplike with (110) terraces. The transition takes place at 480 and 770 °C respectively. The transition at 770 °C is fast, always managing to keep up with the cooling of the sample. The facet planes (10 9 2) and (10 9 $\bar{2}$) are therefore always observed at room temperature on surfaces rotated in the (110) plane around the [001] direction. On the other hand, the transition to surfaces rotated around $[1\bar{1}0]$ relative to the (110) plane, which takes place at low temperature, requires a time of several minutes near the transition temperature. If the sample is cooled more rapidly, the restructuring is incomplete, as is evidenced by the SED patterns.

[1]V. F. Dvoryankin and A. Yu. Mityagin, Kristallografiya **12**, 1112 (1967) [Sov. Phys. Crystallogr. **12**, 982 (1968)].
[2]B. Z. Ol'shanetskiĭ, A. V. Rzhanov, and F. L. Edel'man, Fiz. Tekh. Poluprovodn. **7**, 2312 (1973) [Sov. Phys. Semicond. **7**, 1538 (1974)].
[3]J. J. Lander, Surf. Sci. **1**, 125 (1964).
[4]P. W. Palmberg, Surf. Sci. **11**, 153 (1968).
[5]J. W. Florio and W. D. Robertson, Surf. Sci. **22**, 459 (1970).
[6]B. Z. Ol'shanetskiĭ, N. I. Makryshin, and A. I. Volokitin, Fiz. Tverd. Tela (Leningrad) **14**, 3175 (1972) [Sov. Phys. Solid State **14**, 2713 (1973)].
[7]F. Jona, IBM J. Res. Dev. **9**, 375 (1965).
[8]B. A. Nesterenko, B. Z. Ol'shanetskiĭ, and V. A. Zrazhevskiĭ, Fiz. Tverd. Tela (Leningrad) **16**, 1278 (1974) [Sov. Phys. Solid State **16**, 827 (1974)].
[9]G. A. Somorjai, Surf. Sci. **34**, 156 (1973).