Soviet-era science, translated into English

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CHEMISTRY

1963

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Abstract

Full Text

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CLUSTERS IN HEAVILY DOPED SILICON

(Presented by Academician A. P. Vinogradov, 11 I 1963)

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The method for recording the composition of solids on an MS-7 mass spectrograph with double focusing and a spark ion source is described in detail in ([1], [2]). In ([3]) the results of experiments with graphite are given, and it is shown that the yield of polyatomic carbon molecules (clusters) depends on the state of the structure of the solid phase.

In studying single-crystal silicon on this instrument, we observed, along with atomic and multiply charged ions of the matrix and impurities, molecules from Si_2 to Si_7, and in one sample also Si_8. To resolve the question of the mechanism of formation of these clusters, experiments were carried out with samples of silicon carbide. In the photographs obtained, the pattern of formation of polyatomic ions typical for pure Si and C was not found. In experiments with GaAs and with an Fe–Co–Ni alloy it was established that in the spectra of their salts (after converting these substances into solutions) clusters were absent, although in the solid samples they were recorded.

Fig. 1. Change in the concentration of silicon clusters ($Si_2 \div Si_7$) with the degree of doping of the single crystal with arsenic and boron

These results indicate that the lines of polyatomic ions observed on the photographic plate reflect the structure of the solid, i.e., the corresponding silicon molecules are present in the single crystal and are not products of association from the vapor, as occurs in a Knudsen effusion cell ([4]). It was of interest to study the yield of clusters as a function of the degree of doping of single-crystal silicon. For this purpose samples with an arsenic impurity in the concentration range from 10^{17} to 10^{20} cm^{-3} were analyzed. Before the mass-spectrographic analysis, the concentrations of charge carriers n in them were determined from the Hall effect. The error of its determination did not exceed 5%.

Figure 1 shows the results obtained for the change in the content of silicon

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molecules as a function of the arsenic concentration in the samples. A decrease in the amount of $Si_2 \div Si_7$ with increasing charge-carrier concentration is seen here. As in ([3]), the reproducibility of the results in two parallel experiments on the same sample was a value close to 30% (curves 6 and 7). The maximum difference in cluster concentration for an undoped silicon single crystal (curve 1) and a silicon sample with an arsenic impurity (curves 6 and 7) is almost 100. On the mass spectro-

grams of the samples (curves 5 and 6), the ions SiAs, Si_2As, and Si_3As were recorded. Their content decreases with decreasing arsenic concentration in the specimens. In these same specimens the presence of As_2 molecules was noted. The specimens represented by curves 5, 6 (7), which differ hardly at all in the number of charge carriers, contain different concentrations of clusters. The cluster yield for an undoped silicon single crystal (curve 1) and a specimen containing $1.07 \cdot 10^{17}$ cm^{-3} arsenic (curve 2) is, to a first approximation, the same, although curve 2 is somewhat deformed (apparently because of the presence of As in the specimen) in comparison with curve 1.

Table 1

Sample no.	Curve no. in Fig. 1	Content of doping impurity, determined on the mass spectrograph, N, cm^{-3}	Concentration of charge carriers according to the Hall effect, n, cm^{-3}
Arsenic	**Arsenic**	**Arsenic**	**Arsenic**
1	5	$5 \cdot 10^{20}$	$9.6 \cdot 10^{19}$
2	6–7	$4 \cdot 10^{19}$	$1 \cdot 10^{20}$
3	4	$4 \cdot 10^{18}$	$2.7 \cdot 10^{19}$
4	3	$1.5 \cdot 10^{17}$	$2.7 \cdot 10^{17}$
5	2	$1 \cdot 10^{17}$	$1.07 \cdot 10^{17}$
Boron	**Boron**	**Boron**	**Boron**
6	8	$2.5 \cdot 10^{18}$	$5 \cdot 10^{19}$
7	1	–	$1 \cdot 10^{15}$

Having these data, it was of great interest to see how the content of Si_2–Si_7 would change when the specimen was doped with the acceptor impurity—boron (Fig. 1, 8). It turned out that boron, like arsenic, reduces the content of silicon clusters in the single crystal.

Table 1 gives the results of mass-spectral analysis of the specimens for arsenic and boron content and the concentrations of charge carriers determined in them from the Hall effect.

The As contents given in Table 1 for the silicon specimens (Nos. 1 and 2) do not agree with the results of radioactivation analysis, but within a factor of 1.5

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Fig. 2. Dependence of the concentration of charge carriers (n) on the arsenic content in silicon single crystals (N): 1 —theoretical, 2 —experimental

Figure 2: Fig. 2. Dependence of the concentration of charge carriers (n) on the arsenic content in silicon single crystals (N): 1 —theoretical, 2 —experimental

Fig. 3. Simplified unit cells of silicon: a —normal, b —deformed

Figure 3: Fig. 3. Simplified unit cells of silicon: a —normal, b —deformed

they agree with the chemical-spectral data. Here, too, attention is drawn to the discrepancy between the concentration of charge carriers and the content of arsenic and boron. It begins to appear already in specimen No. 4 and increases with increasing As content (Fig. 2). For specimen No. 3, for example, only 1/7 of the charge-carrier concentration can be attributed to arsenic, and in doping with boron (specimen No. 6) about 1/20. In specimen No. 5, the concentration of charge carriers and the arsenic content determined on the mass spectrograph coincide. Specimens Nos. 2 and 1, as it turned out, contain unequal amounts of arsenic. The interval of change in the yield of silicon clusters from specimen No. 7 to specimen No. 2 (curves 1 and 6) is possibly maximal, since increasing the impurity—arsenic—to $5 \cdot 10^{20}$ cm^{-3} (specimen No. 1) again leads to an increase in the yield of $Si_2 \div Si_7$ (curve 5, Fig. 1), while the concentration of charge carriers decreases (Fig. 2).

Fig. 2. Dependence of the concentration of charge carriers (n) on the arsenic content in silicon single crystals (N): 1 —theoretical, 2 —experimental.

For a qualitative explanation of the results obtained, it is necessary to ascribe to silicon clusters a special position in the lattice of the single crystal, as is shown in simplified form in Fig. 3, . Here atoms 1 and 2, which make up the cluster, must have a stronger bond with one another than the bonds between the remaining atoms in the cell. Such an assumption will be justified if we admit that in the solid phase there exist the most energetically probable formations found in the gaseous phase, as shown in work ([4]). Similar considerations can also be carried out for more complex clusters.

In a spark ion source, during destruction of the sample, the less strong bonds will be broken, whereas clusters will be recorded in the form of heavy ions. When a silicon single crystal is doped with arsenic or boron, the atoms of the latter, forming a substitutional solid solution, redistribute the energy in the lattice, as a result of which the probability of bond rupture in the molecule increases and the yield of clusters decreases. One can also imagine a case in which an As atom replaces atom 2 in the lattice (Fig. 3, *b*). In this case the Si_2 cluster will be "destroyed" owing to formation of the SiAs complex, which was indeed observed experimentally. It is easy to see that at very high arsenic concentrations ($N > 10^{20}$ cm^{-3}) new clusters of the As_2 type (Fig. 3), which were in fact observed in the spectrum of sample No. 1, will begin to form.

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Fig. 3. Simplified unit cells of silicon: *a* —normal, *b* —deformed.

Let us note that the possibility of the existence of similar clusters, using P_2 as an example, was predicted earlier ([5]), but they could not be observed experimentally, since samples with a low concentration of the phosphorus impurity were studied. For a full understanding of the experimental results obtained, it is necessary to explain the observed differences in the values of n and N (see Table 1). Here one must assume that the decrease in the number of clusters in doped silicon is the cause of the introduction of defects into the structure, with the formation of local donor levels in the forbidden band with a relatively low ionization energy.

In conclusion, we consider it our pleasant duty to thank Acad. A. P. Vinogradov, Corresponding Member of the Academy of Sciences of the USSR N. P. Sazhin, and Prof. E. S. Makarov, who took part in the discussion of this work and offered a number of valuable suggestions and comments at various stages of its execution.

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Received
24 XII 1962

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