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Abstract

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PHYSICS

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ON THE QUESTION OF ANOMALOUS PLASTICITY OF NEAR-SURFACE LAYERS OF SEMICONDUCTOR CRYSTALS

(Presented by Academician N. N. Rykalin, 21 II 1969)

The question of the possibility of low-temperature plastic deformation of covalent crystals with a diamond lattice has been discussed in the literature for quite a long time ([1–10]). Usually, for various types of concentrated loading the temperature threshold of brittleness T_{cr} is, for Si, $500 \div 550°$, and for Ge about 250°C ([2]). In bulk loading methods (tension, compression, torsion, bending), T_{cr} is somewhat higher—of the order of $650 \div 700°$ for Si and about 400° for Ge. Recently data have been obtained on the possibility of plastic deformation of Si at lower temperatures: at 300° ([2,5]), 20° ([6,7]), and even at the temperature of liquid nitrogen ([7,8]). Thus, for example, in papers ([7,8]) the authors, having proposed a new method of concentrated loading of brittle crystals through a gasket of plastic metal (“soft indentation”), proved by various experimental methods (hot microhardness and submicrohardness methods, metallographic examination by etch pits, polarization-optical and transmission electron microscopy) the possibility of plastic deformation of Si below 500°, down to the temperature of liquid nitrogen, in a thin near-surface layer with a depth from fractions of a micron at −196 and 20° to several microns at higher temperatures. At the same time, no signs of brittle fracture were observed.

One of the most important questions in this problem is the determination of the stress level at which low-temperature plastic deformation of diamond-like semiconductors proceeds, since, although the possibility of their plastic deformation below the brittle-fracture temperature had previously been allowed by individual authors, it was believed ([2,3,9]) that it could occur either as macroplastic deformation at very high stresses close to the theoretical shear strength of the crystal (450–500 kg/mm^2 according to the data of ([9,10])), or as microplastic deformation necessary for the nucleation of a brittle crack ([3,6]). Apparently, in the second case as well, the nucleation of microcracks and the local plastic deformation preceding them will occur only if stresses close to the theoretical strength are reached.

In paper ([8]), for the temperature interval from −196 to 550°, a calculation was

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Fig. 1. Temperature dependence of the critical shear stress τ_{cr} in Si under "soft loading"

Figure 1: Fig. 1. Temperature dependence of the critical shear stress τ_{cr} in Si under "soft loading"

made of the critical shear stresses at which, in the contact under the conditions of "soft indentation" loading, plastic deformation began in the near-surface layer of Si. In the initial state Si was dislocation-free. As the criterion for the onset of plastic deformation, the appearance on the Si surface after loading of a dislocation density of the order of $5\cdot 10^1$–10^2 cm^{-2} was taken. The stresses in the contact were calculated by the method proposed in paper ([11]). The applicability of the problem of deformation of a plastic bar on a rigid base ([11]) to the process of "soft indentation" was proved by photoelasticity experiments during loading of Si through Pb along the $\langle 111\rangle$ axis at 20° with its simultaneous examination in an infrared microscope ([8]). The final results of the calculation of the critical shear stresses causing plastic deformation in the near-surface layer of Si, as a function of temperature, are presented in Fig. 1.

On considering Fig. 1, two main conclusions can be drawn. First, Si and other diamond-like semiconductors (control experiments were also carried out on Ge) can deform at stresses considerably lower than the theoretical strength limit. In this case τ_{cr} is 1.5-2 orders of magnitude lower than $\tau_{\text{theor}} = 450$–$500$ kg/mm^2 ([9,10]). Second, there is a clear temperature dependence of τ_{cr}, which had not been detected earlier, for example in hot microhardness experiments ([2]). From Fig. 1 it is seen that in the temperature range from -196 to 200° a linear dependence is observed, while in the temperature range 350–550° the dependence of τ_{cr} on temperature is exponential.

To estimate the activation energy of dislocation motion, the formula proposed in ([12]) was used:

$$\tau_{\text{cr}} = \sqrt[3]{\frac{3B\dot{\varepsilon}kT}{V}}\, e^{U/3kT} = \alpha e^{U/3kT},$$

where α is a certain coefficient depending on the deformation rate $\dot{\varepsilon}$, the magnitude of the activation volume V, and the parameter B, which takes into account the type of material and the loading method.

Fig. 1. Temperature dependence of the critical shear stress τ_{cr} in Si under "soft loading"

The value of the activation energy determined in the temperature interval from 350 to 550°, $U = 0.84 \pm 0.1$ eV, is considerably lower than the literature data: $U = 1.93$ eV for n-type Si and $U = 2.34$ eV for p-type Si ([13]), which, it is true, were obtained for bulk deformation and at higher temperatures. Apparently, precisely this circumstance may explain the indicated discrepancy. Closest to

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the activation-energy value found is the value $U = 1.4$ eV, obtained in ([2]) from relaxation curves of residual stresses from microhardness impressions by the method of infrared polariscope in an analogous temperature interval.

It is known ([12]) that from the temperature dependence of the critical shear stress one can determine the value of the activation volume $V = b^3 lS = U/\tau'_{cr}$, where b is the Burgers vector; l is the length of a double kink of a dislocation; S is the half-width of the Peierls–Nabarro barrier; U is the activation energy of dislocation motion; and τ'_{cr} is the critical shear stress at absolute zero, which can be obtained by extrapolating the curve in Fig. 1. An estimate of this quantity from the data of Fig. 1 gave the value $V = 480 \cdot 10^{-24}$ cm^3, which is almost an order of magnitude higher than for bulk deformation ([12]). If it is assumed that the increase in the activation volume in the present case is due not only to an increase in l, but, at least, to an increase in both parameters l and S, then this may indicate an increase in the width of the Peierls–Nabarro barrier, i.e., a certain smoothing of the potential relief at the crystal surface.

An analysis of the literature data on the role of the surface in the general process of macroplastic deformation of crystals also indicates a lower shear stress at the crystal surface; in particular, the Fischer surface source ([14]), when the image forces are taken into account, operates at stresses two times smaller than in the crystal bulk. If, moreover, various schemes of heterogeneous nucleation of dislocations at surface steps, oxide films, etc., are taken into consideration, the shear stress will be still lower. In addition, literature data, in particular the works ([13,15]), indicate a higher rate of dislocation motion at the crystal surface than in the bulk. Thus, the low critical shear stress, the small value

the activation energy, the large value of the activation volume, and the higher mobility of dislocations indicate the anomalous character of the mechanical properties in the near-surface layer of Si. Attention is drawn to the fact that the anomalous mechanical properties are manifested precisely in the thin near-surface layer of the crystal. An estimate of the depth of the anomalous near-surface layer in Si, carried out in work ([8]), shows that its magnitude ranges from hundredths and tenths of a micron at $T = -196$ and 20° to several microns at higher temperatures.

The special deformability of the near-surface layer in comparison with the bulk of the crystal is confirmed in a number of works on abrasive treatment of semiconductors ([3], [4]), in which it was shown that, on passing to a definite degree of abrasive dispersion (for Si, of the order of $0.25\,\mu$ ([4])), brittle cracks can be completely avoided and clean individual dislocations can be obtained. With coarser abrasive particles, brittle fracture is usually observed ([3], [4]). An analogous regularity is also manifested under static loading of semiconductor crystals, when purely plastic deformation can occur only at a strictly definite magnitude of the load ([1], [6]), whereas at a larger load, which correspondingly involves deeper layers of the near-surface layer in plastic deformation, along with the formation of dislocations a process of brittle fracture is observed ([3]).

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Finally, it should be noted that it is precisely in the near-surface layers of crystals (of the order of 2–5 μ for Si and Ge and not more than 15 μ for GaAs) that photomechanical ([15]), electromechanical ([16]), and concentration ([15]) effects are usually manifested. Although the nature of these effects has not yet been precisely established, almost all explanations of them reduce to the supposition of a lowering of the Peierls barriers under the action of one or another external factor (electric field, illumination, etc.). Since in the present work the indicated external factors were absent, on the basis of the results obtained it may be assumed that a lowered value of the Peierls–Nabarro barriers is to some extent physically inherent in the surface, while an electric field, illumination, and doping can enhance this effect, i.e., promote the manifestation of the anomaly of the mechanical properties at the crystal surface, just as in the present case this is promoted by the specific conditions of the method of loading the crystal through a plastic gasket. This supposition is confirmed by the small value of the activation energy for dislocation motion and the large value of the activation volume obtained in the present work, which indicate a certain smoothing of the potential relief at the surface of the crystal.

One of the possible explanations of the results obtained may be connected with the presence, at the surface of a semiconductor crystal, of a Debye layer with an increased carrier concentration and a corresponding value of space electric charge ([17]), and with its influence on the magnitude and shape of the potential relief of the lattice at the crystal surface. The magnitude of the Debye layer and of the corresponding space charge, as is known, is determined by the concentration of surface impurities and Tamm levels, as well as by the concentration of intrinsic carriers in the bulk of the crystal ([17]). This electric charge causes bending of the energy bands at the crystal surface and, apparently, can reduce the value of the Peierls barrier and also interact with charged dislocations, facilitating their motion ([15]).

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