On the Physical Nature of a Photomechanical Effect

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Abstract—A photomechanical effect was studied in single-crystal Si by a unified method. The dependences of the photomechanical effect on the spectrum and intensity of light, the residual photomechanical effect (the persistence of crystal softening for some time after the termination of indentation), the effect of illumination on microhardness anisotropy, and the temperature dependence of the photomechanical effect were studied. Based on the experimental results and on the analysis of relevant published data, the correlation between the photomechanical effect and the corresponding density of photogenerated nonequilibrium carriers (so-called antibonding quasiparticles) is determined. This correlation suggests a mechanism according to which, in covalent crystals, microhardness decreases mostly owing to chemical bond weakening and isotropization caused by the photogenerated antibonding quasiparticles. © 2001 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

The photomechanical effect (PME) [1], which is actually a photoinduced change in material microhardness (MH), has been studied previously [1–8]. However, no explanation of the physical nature of this effect has been offered. This is probably due to a discrepancy in the experimental data obtained by different techniques under different conditions. In this paper, we report the results of studying the PME in Si by a single method, which gives an insight into the physical nature of the effect of illumination on microhardness.

The MH measurement is known to involve material damage leading to a displacement of a certain amount of the studied material under the indentor pressure. By producing a decrease in MH, light facilitates the material displacement, which means an increase in the mobility of atoms relative to each other, i.e., a change in atomic interaction. The origin of the photoinduced increase in the atomic mobility is clarified by a new concept of atom displacement in solids proposed in [9, 10]. The main idea of this concept is outlined below.

The method of linear combination of atomic orbitals (LCAO) applied to electronic states in semiconductors in a tight binding approximation yields two energy values [11]: the lower energy corresponds to bonding states and the higher, to antibonding states. The top of the valence band, which consists of bonding orbitals, corresponds to electronic P states, while the conduction band bottom, to electronic S states (Fig. 1). Consequently, each electron transition from the valence to the conduction band, i.e., a transition from a bonding to an antibonding state, involves a corresponding change in the electron quantum state. In other words, the binding energy decreases, and the distribution of negative charge changes around the atoms adjacent to a free electron or to a hole involved in thermal motion. Since the S orbital exhibits spherical symmetry and the P orbital has an oriented dumb-bell-like electron cloud, an electron transition from the P state increases the specific weight of the S state in the vicinity of an atom (Fig. 1). Therefore, the more conduction electrons and holes are induced in crystal, the larger is the decrease in the binding energy and in the fraction of the fixed-orientation P bonds. Consequently, the atoms acquire an additional degree of freedom, and their mobility relative to each other becomes higher [10]. It is worth noting that the local energy levels introduced by defects within the band gap are actually bonding and antibonding orbitals for acceptor and donor levels, respectively. Hence, the electrons in the conduction band, at donor levels and holes in the valence band, and at acceptor levels appear to be antibonding quasiparticles. The experimental data presented below illustrate the crucial role of antibonding quasiparticles in PME.

2. EXPERIMENTAL

We used dislocation-free single-crystal n-Si samples, with resistivity $\rho = 200 \Omega \text{cm}$, Sb-doped to a concentration of $N_d = 2.3 \times 10^{13} \text{ cm}^{-3}$. The samples were cut in the (100) surface plane with a disorientation no larger than 0.3°. The microhardness was measured using a Durimet indenter equipped with a standard tetrahedral Knoop pyramid. Before indentation, the sample surfaces were chemically and mechanically treated with subsequent vacuum annealing. The sample was unloaded some time after the light has been switched off. In all the experiments, the large diagonal of the Knoop pyramid coincided with the (100) direction of the studied (100) plane. The necessity of the last two conditions will be clarified in Sections 4 and 5. The thickness of SiO$_2$ film on the studied Si surface was
measured by an ellipsometer to be about 30 Å. In preliminary testing, the SiO₂ layers less than 60 Å thick were shown to produce no effect on the MH load curve. Nonmonochromatic light was produced by tungsten-filament lamps of type K21-150. The lamps were regularly arranged, at an 8-cm distance from the studied sample. The luminous flux made an angle of 60° with the normal to the sample surface. To obtain light with photon energy \( hv > \Delta E_g \), we employed a monochromatic light source, an LGN-404V He–Ne laser operating at a \( \sim 0.64 \mu \text{m} \) wavelength. To vary the intensity of light, we used neutral filters and varied the number of lamps. To eliminate thermal effects, the lamps, filters, and the studied sample were cooled with blowing air. The temperatures of the illuminated surface were measured, and the testing of samples in the dark at the same temperatures demonstrated that the additional heating does not effect MH, thus indicating a nonthermal origin of the observed PME.

3. DEPENDENCE OF PME ON THE SPECTRUM AND INTENSITY OF LIGHT

Figure 2 shows the results of measuring PME as a function of light spectrum. Curve 2 in Fig. 2 corresponds to the action of laser irradiation on the studied crystal. It is obvious from the plot that PME exists in a certain region of the load \( (P < 100 \text{ g}) \), while, as the load increases, the curves obtained during irradiation and in the dark merge together. The photoinduced decrease in MH is noticeable if the indentor penetrates into the surface layer to a depth comparable with inverse absorption coefficient \( 1/\alpha \), since most of the antibonding quasiparticles are produced within this layer (farther on, their concentration drops exponentially with the depth). The dependence of silicon MH on the radiation intensity for \( hv > \Delta E_g \) is plotted at the inset in Fig. 2 (curve 2). Here, the linear drop gives way to saturation. This behavior can be explained by the following considerations. After a certain intensity of light is exceeded, the photogenerated quasiparticles soften the thin surface layer to the extent that it does not contribute to the material MH that, in this case, is defined by the deeper layers where quasiparticles are practically absent. We have also observed PME in the crystals irradiated with light with photon energy \( hv < \Delta E_g \) (Fig. 2, curve 3). In this case, the irradiation of Si results in a decrease in MH within the entire range of the loads used in the experiment. Indeed, the decrease in MH with increasing intensity of light with photon energy \( hv < \Delta E_g \) is nearly linear (inset in Fig. 2, curve 1). Therefore, in this case, PME is independent of the indentor penetration depth. This fact can be attributed to the following. Since the studied crystal is transparent to radiation with \( hv < \Delta E_g \), the observed PME is due to the absorption of light by defects produced by the indentor. Because of a low absorption, the radiation penetrates into the entire damaged region, no matter how deep the indentor may penetrate during the experiment. As a result of indentation, a considerable crystal disordering occurs: a defect layer forms around the indentor and extends deep into the crystal. As is known [12], the band gap of a highly disordered semiconductor contains the tails of the density of states, which in their turn lead to a change in the optical absorption of the damaged region compared to an undamaged crystal. The tails of the valence and conduction bands consist of

![Figure 1](image1.png)

**Figure 1.** Energy bands of approaching atoms (\( r \) is the internuclear separation) and the change in the energy and electron density distribution of a chemical bond as a result of electron transition from a bonding to an antibonding state.

![Figure 2](image2.png)

**Figure 2.** Microhardness vs. load curve in Si (\( P \) is the indentor pressure) (1) in the dark, under irradiation with photons (2) with \( hv > \Delta E_g \) and (3) with \( hv < \Delta E_g \). The accuracy is the same for all the curves. Inset: microhardness \( H_K \) versus intensity of light in the case of irradiation with (1) photons with \( hv > \Delta E_g \), (2) photons with \( hv > \Delta E_g \) and (3) white light. \( I \) is intensity in arbitrary units corresponding to the number of light sources, \( I = 0 \) corresponds to darkness.