2001

Bulk stress due to surface damage of crystalline silicon and germanium

P. Fisher  
*University of Wollongong, pfisher@uow.edu.au*

R. Vickers  
*University of Wollongong, rv@uow.edu.au*

http://ro.uow.edu.au/engpapers/143

Publication Details  
Bulk stress due to surface damage of crystalline silicon and germanium

P. Fisher and R. E. M. Vickers
Department of Engineering Physics and Institute for Superconductivity and Electronic Materials, University of Wollongong, Wollongong, New South Wales 2522, Australia

(Received 6 August 2001; accepted for publication 4 September 2001)

It is found that abrading two opposing surfaces of either crystalline Si or Ge samples results in homogeneous, uniaxial stress throughout the bulk perpendicular to the damaged surfaces. The latter are chosen to coincide with simple crystallographic planes. This conclusion is reached by analyzing the splittings, intensities, and polarizations of the absorption lines of the Lyman series of bulk shallow impurities in the abraded semiconductors. This effect has been observed for samples which range in thickness, t, from 1 to 3 mm, the internal stress being proportional to \( t^{-1} \).

A force, \( \mathbf{F} \), applied to crystalline Si shifts the conduction band minima by

\[
\epsilon_j = \pm \Xi_j (s_{11} - s_{12}) S \cos^2 \theta_j - 1/3, \quad j = 1, 2, \ldots, 6
\]

where \( \theta_j \) is the angle between \( \mathbf{F} \) and the direction in k space of the jth minimum.\(^5\) In Eq. (1), \( \Xi_j \) is the shear deformation potential constant of each of the six equivalent band minima, \( s_{11} \) and \( s_{12} \) are elastic coefficients of the crystal, while \( S \) is the stress. The positive sign is for tension and the negative sign for compression. Thus, for \( \mathbf{F} || [100] \), \( \epsilon_{1,2} = -2 \epsilon \) and \( \epsilon_{3,4,5,6} = -2 \epsilon = \Xi_j (s_{11} - s_{12}) S / 3 \). Here, the conduction band minima along [100], [110], [010], [001], and [001] are labeled 1, 2, 3, 4, 5, and 6, respectively. Also, the electric dipole selection rules for transitions from the singlet ground state,\(^8\) for \( \mathbf{E} . \mathbf{F} \), permit transitions to both stress-induced \( m = \pm 1 \) states but to only the higher energy one of the two stress-induced \( m = 0 \) excited states; here \( \mathbf{E} \) is the electric field of the radiation.

The pattern of the spectrum in Fig. 1, from the damaged sample, matches that obtained if an applied, homogeneous compressive force were along a (100) direction with \( \mathbf{E} . \mathbf{F} \).\(^8,10\) Thus, it is concluded that the surface damage produces a compressive stress, \( S_{eff} \), throughout the bulk of the sample, perpendicular to the optical faces. Since the radia-

---

\(^8\)Electronic mail: peter_fisher@uow.edu.au
In keeping with the above considerations since, for $P$ estimated to be 0.94 for Ge is shown in Fig. 2 for the same ingot, illustrating the reproducibility of the process. The data are the splittings obtained from two samples cut from the optical faces for Si has not yet been studied but it has for Ge. Also, for the latter, the case of $P_{111}$ components of the Lyman spectra of the acceptors confirms the conclusions deduced from the behavior of the $P$ lines for $\{100\}$, $\{110\}$, and $\{111\}$ optical faces. Also, it was found that, for a given thickness of Ge, the value of $s_{\text{eff}}$ is estimated to be 0.94 ± 0.01 MPa.

A phosphorus-doped Si sample with $\{111\}$ optical faces was examined. No splitting of the $P$ lines was observed, in keeping with the above considerations since, for $P_{111}$, Eq. (1) predicts that $v_{ij} = 0$ for all $j$. This is what is obtained experimentally for $P_{111}$, applied externally.

The case of $\{110\}$ optical faces for Si has not yet been studied but it has for Ge. Also, for the latter, the $\{111\}$ and $\{100\}$ optical faces have been examined. The shifts of the conduction band minima of Ge are given by an equation similar to Eq. (1). For this material there are four equivalent conduction band minima located at the zone boundaries along $\{111\}$ directions, and, hence, for donors, with $P_{100}$ no line splittings should occur while they should for $P_{111}$. These characteristics are those observed experimentally when such forces are applied externally, and are what are seen for spectra obtained from samples of phosphorus-doped Ge with $\{100\}$ and $\{111\}$ optical faces abraded with No. 400 SiC powder in water slurry. The dependence on $t^{-1}$ of the splitting of the $P_{111}$ components of $P$ for Ge is shown in Fig. 2 for $\{111\}$ faces. Included in these data are the splittings obtained from two samples cut from the same ingot, illustrating the reproducibility of the process. The line through the data is a least squares fit with a slope of 1.70 ± 0.04 cm$^{-1}$ mm.

From the splitting of the $P$ lines, $s_{\text{eff}}$ is estimated to be 0.92 ± 0.02 MPa for a sample of Ge with $t = 1.92$ mm; this is remarkably close to that obtained for the Si sample with $t = 1.91$ mm whose spectrum is given in Fig. 1. Unperturbed spectra for Ge could be obtained by subjecting the abraded samples to ultrasonic treatment (UST). The samples were immersed in a beaker of distilled water placed in either a 30 or 43 kHz ultrasonic bath filled with water. During the UST, fine particles collected in the bottom of the beaker and, using a scanning electron microscope, were identified to be Ge. The splittings of the donor states with the time of UST is exponential. Subsequently, we have learned that Ge is etched by water. We found that in this case the reduction in the splitting was very much slower than under UST; also no detritus accumulated.

The phosphorus-doped Ge samples examined contained shallow acceptors. The splittings and intensities of the stress components of the Lyman spectra of the acceptors confirmed the conclusions deduced from the behavior of the $P$ lines for $\{100\}$, $\{110\}$, and $\{111\}$ optical faces. Also, it was found that, for a given thickness of Ge, the value of $s_{\text{eff}}$ is essentially the same for all three faces.

The results in Fig. 2 demonstrate that $s_{\text{eff}}$ is proportional to $t^{-1}$. Since the effective strain, $s_{\text{eff}} = \Delta s_{\text{eff}}/t$, is proportional to $s_{\text{eff}}$, this implies that $\Delta s_{\text{eff}}$ is constant, independent of $t$. Thus, the surface damage inflicted by abrasion with a grit of a given size leads to a $\Delta s_{\text{eff}}$ which is independent of $t$. It should be noted that $\Delta s_{\text{eff}}$ is not the thickness of the damage inflicted on the surfaces.

Clearly, after abrasion the surfaces are not in equilibrium and, for Ge at least, the elastic energy is released relatively rapidly by UST. Apparently at the power levels and frequencies of the baths used, coupling with acoustic modes in the strained Ge surfaces is sufficient to cause particles to become detached. This extreme reconstruction of the surface did not occur for Si because, it is conjectured, of the stronger covalent bonds which limit the vibrational amplitude of the surface atoms.

The very small, homogeneous stress obtained using the above procedure has provided a better comparison between theoretical and experimental stress-induced effects with more reliable deformation potential constants being obtained than previously. This application is being exploited further. Extension of the UST to higher frequencies and power is planned as is the controlled etching of samples to determine the depth of the damage producing the internal stress for correlation with other determinations.

In conclusion, it was shown that the extensive surface damage produced by abrasion of surfaces of crystalline Si and Ge with carborundum generates amazingly homogeneous, internal stress perpendicular to the damaged surfaces throughout bulk thicknesses of at least 3 mm. This was deduced by analyzing the sharp Lyman spectra of bulk, shallow impurities of samples with and without surface damage. Similar results have also been obtained for Si and Ge using alumina as the abrading material.

The authors wish to thank D. C. Lau for assistance with the literature survey. The work was supported by the University of Wollongong Board of Research and Postgraduate Studies. The silicon transmutation was carried out under an Australian Institute of Nuclear Science and Engineering grant in conjunction with the Australian Nuclear Science and Technology Organization.
9 The phosphorus-doped Si was obtained by neutron transmutation of essentially undoped Si.
11 V. J. Tekippe, H. R. Chandrasekhar, P. Fisher, and A. K. Ramdas, Phys. Rev. B 6, 2348 (1967). (For Si the value of $\Xi_u$ is 8.77 ± 0.07 eV.)
15 E. E. Haller (private communication).