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OPTICAL CONSTANTS OF PURE AND HEAVILY DOPED SILICON AND GERMANIUM: ELECTRONIC INTERBAND TRANSITIONS

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The technique of Fourier analysis ellipsometry has been applied to pure and heavily doped n- and p-type Ge and Si (doping up to $\approx 10^{20}$ cm^{-3}) to obtain accurate spectra of ε_1 and ε_2. We have studied the shift and broadening of the E_1 (3.4 eV in Si, 2.1 - 2.3 eV in Ge) and E_2 ($\sim$4.3 eV in both) with doping. All these peaks shift to lower photon energies and broaden with doping. These shifts amount to $\sim$0.05 eV for dopings of 10^{20} cm^{-3}. The results are discussed in terms of the perturbation produced by the ionized impurities.

The effects of temperature on the fundamental electronic spectra of semiconductors have been profusely studied.[1,2] Singularities (critical points) in these spectra shift and broaden with increasing temperature. The disorder introduced by doping with "hydrogenic" impurities produces similar effects. These effects, however, are smaller. They have been much less studied [3-6] than those of temperature: the range of doping possible is severely limited by the solubility of the impurities ($\lesssim$1%). We present here the optical constants of pure and heavily doped Ge and Si as determined with an automatic rotating analyzer ellipsometer.[7] The position of the E_1 and E_2 critical points and their broadening have been determined from the second derivative spectra. They all shift to lower energies with doping.[3]

The real (ε_1) and imaginary (ε_2) parts of the dielectric constant of pure and p-type (B-doped, 4 x 10^{20} holes/cm^3) Si are shown in Fig. 1. The samples were polished with Syton and a Br-methanol solution.[8] They were etched in the N_2-flushed measurement chamber, following the prescription in Ref. 8. This procedure was repeated until the highest values of ε_2 at E_2 (Fig. 1) were obtained. The treatment was found to be reproducible to within $\Delta\varepsilon_2 = \pm 2$ at the E_2 peak. The red shift of E_2 with doping, and its broadening, is clearly seen in Fig. 1, also the broadening of E_1. In order to see the red shift of the critical frequency E_1 we must look at the second derivative spectrum of ε_2 in Fig. 2. We recognize by sight a red shift of E_1 of $\sim$0.05 eV. A line width analysis of this critical point yields a Lorentzian broadening parameter Γ = 0.06 eV for the pure material and 0.09 eV for the heavily doped one. Similar analysis yields a red shift of 0.05 eV for E_2. The Lorentzian broadenings are 0.05 eV and 0.065 eV in the pure and heavily doped case, respectively. The spectra of ε_1 and ε_2 for a pure and a heavily doped Ge sample, treated as discussed in [8], are shown in Fig. 3. The red shifts for the heavily doped sample ($\sim$0.04 eV for E_1, 0.03 eV for $E_1 + \Delta_1$ and 0.04 eV for E_2) are seen in Fig. 4. Their corresponding broadening parameters are $\Gamma(E_1) = \Gamma(E_1 + \Delta_1) = 0.055$ eV, $\Gamma(E_2) = 0.10$ eV for pure Ge, and $\Gamma(E_1) = \Gamma(E_1 + \Delta_1) = 0.08$ eV, $\Gamma(E_2) = 0.11$ eV for the heavily doped sample.

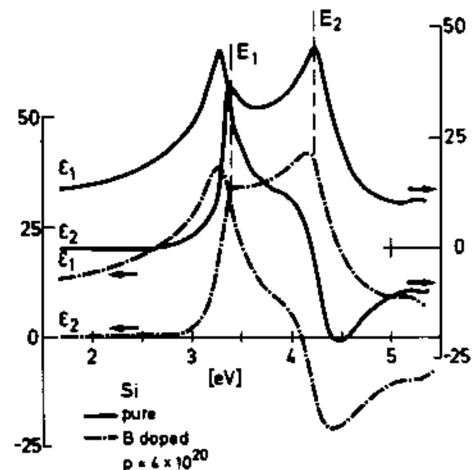

Figure 1 : ε_1 and ε_2 for undoped and heavily doped (4 x 10^{20} holes x cm^{-3}) silicon at room temperature.

The critical energies E_1, $E_1 + \Delta_1$ and E_2 found from measurements for many samples are shown in Figs. 5 and 6. These shifts agree with the early results of [3] and with similar results for GaAs.[5]

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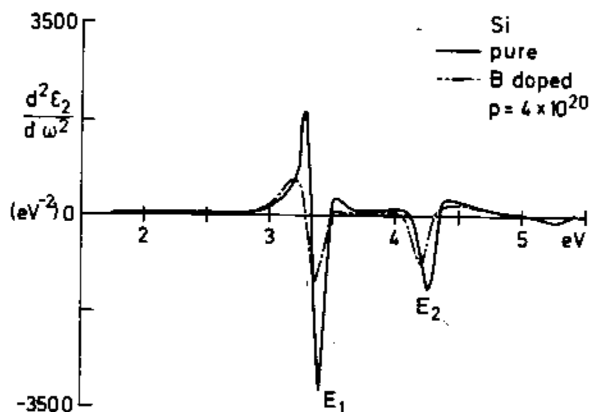

Figure 2 : Second derivative spectra of the ε_2 in Fig. 1. The derivatives were calculated with a mesh of 0.01 eV.

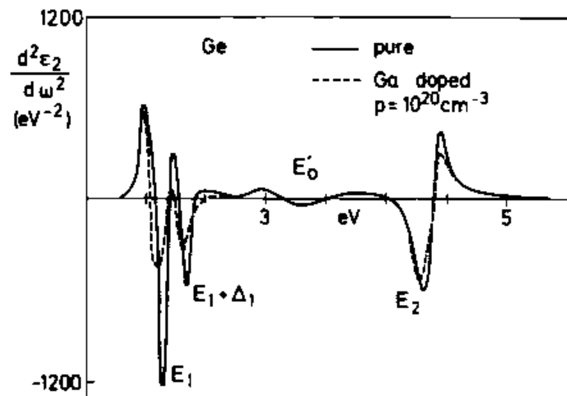

Figure 4 : Second derivative spectra of the samples in Fig. 3. The derivatives were calculated with a mesh of 0.02 eV.

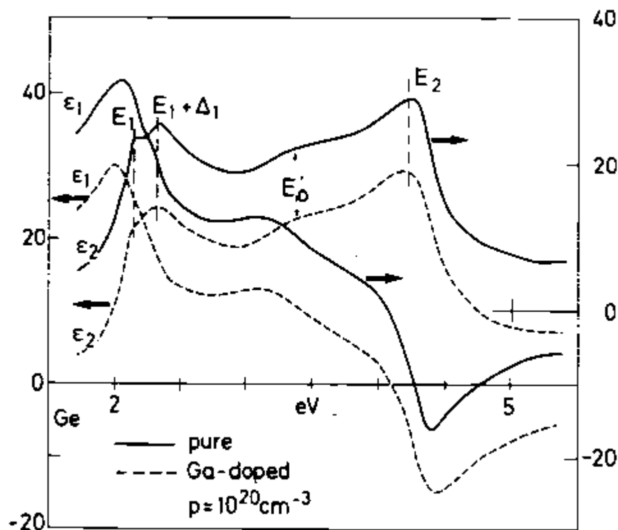

Figure 3 : ε_1 and ε_2 for undoped and heavily doped (10^{20} holes x cm^{-3}) germanium at room temperature.

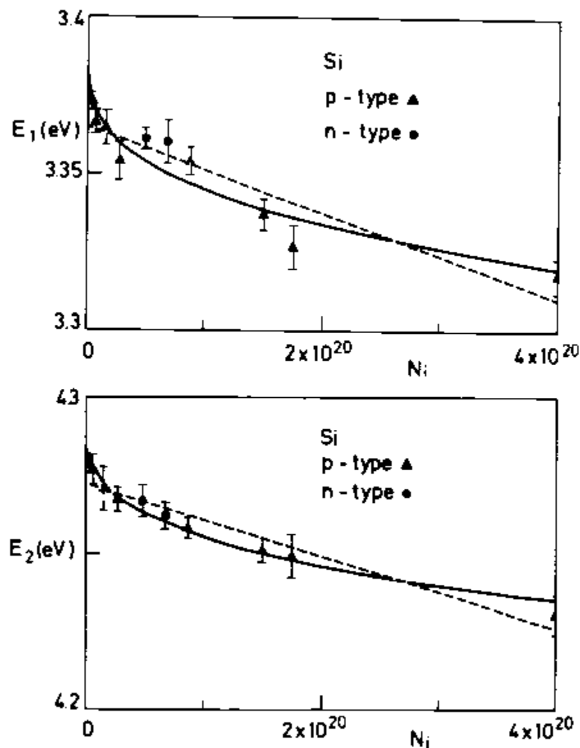

Figure 5 : Energies of the E_1 and E_2 critical points of Si at room temperature vs. doping. The dashed line is a linear fit while the solid line represents a fit $\propto N_i^{1/3}$. The data for both n- and p-type samples were fitted simultaneously.

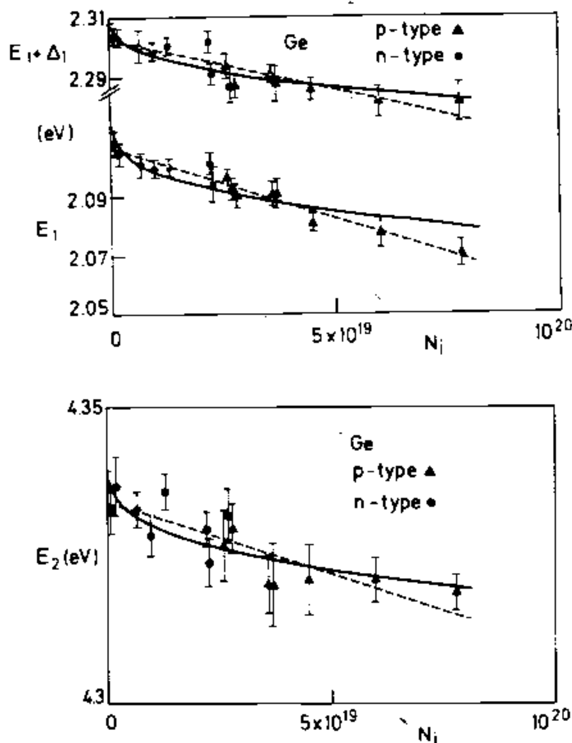

Figure 6 : Energies of the E_1, $E_1+\Delta_1$, and E_2 critical points of Ge at room temperature vs. doping. The dashed line is a linear fit while the solid line is a fit $\propto N^{1/3}$.

The lowest order contributions to the shifts of Figs. 5 and 6 arise from the change in the "virtual crystal" potential (first order perturbation) and from second order terms involving a virtual intermediate state.[9] The former, proportional to impurity concentration N_i, has been estimated by pseudopotential calculations using for the perturbation potential the antisymmetric potential of GaAs.[10] We find it to be an order of magnitude smaller than the data of Figs. 5 and 6. Note that this contribution should change sign in going from n- to the p-type case. There is no evidence for that in Figs. 5 and 6 where data for n- and p-type material have been plotted together vs. N_i. We are in the process of calculating the second order terms which are also responsible for the increase in Γ. The contributions of these terms to the energy shifts can be roughly divided into two categories: terms with large q-transfer to the intermediate state and with small q-transfer. The former yield a shift proportional to N_i, the latter a $N_i^{1/3}$ contribution (at low temperatures so that $kT < E_F$) because of screening by the free carriers. We have thus fitted Figs. 5 and 6 with curves proportional to N_i and to $N_i^{1/3}$. The fit is nearly equally good in both cases. In the absence of more heavily doped samples due, in part, to the solubility of the impurities, the type of dependence on N_i must be clarified through calculations. Our data also agree, within error, with the $N_i^{1/3}$ dependence of the E_0 gap of GaAs after removing the Burstein-Moss shift which is not present in our case.[11]

We have not seen the broadening of the E_1 edge of As-doped Si reported in [6] for dopings up to 5×10^{19}. Our results look the same, up to this concentration, for As as for P or B. We suspect the results of [6] are due to peculiarities of the ion implantation.

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