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ABSORPTION EDGE OF ULTRAHEAVILY DOPED Si

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The absorption edges of P- and As-ion implanted, laser-annealed thin SOS films have been measured between 1.5 and 3.5 eV. The strong increase in absorption reported by Jellison et al. for As-doped samples has been shown to be spurious. It has nevertheless been found that these edges shift towards the red by ~0.3 eV for either P or As doping of concentration $N_i \simeq 2\times10^{21}$ cm^{-3}. These shifts are discussed in terms of the perturbation produced by the impurities on the band structure.

In a recent paper Jellison et al.[1] reported ellipsometric measurements on thin single crystal silicon films produced by implantation followed by pulsed ruby laser annealing. From these data, the room temperature absorption spectra of several films, doped with As up to 3.2×10^{21} ions/cm^3 in the region between 1.5 and 4 eV were obtained. A strong increase in the absorption below 3.3 eV (the lowest direct gap of Si) was found with increasing dopant concentration. This effect, which was largely absent for either P or B doping, was attributed to the effect of the 3d electrons of As on the band structure of silicon.

Because of the well-known drawbacks of ellipsometric techniques in the region of small absorption, and in order to check the results in Ref. 1, we have performed direct absorption measurements on SOS (silicon on sapphire) films which were implanted with either P or As ions and laser annealed with an excimer laser. The transparency of the substrate and the thinness of the SOS films (0.770 μm) enabled us to follow the absorption edge of the implanted region to absorption coefficients from $\sim 3 \times 10^3$ to 4×10^5 cm^{-1}. The observed red shift of the absorption edge with increasing doping (~0.3 eV for the $N_i \simeq 2 \times 10^{21}$ cm^{-3}) was nearly the same for equal concentrations of either P or As and much less than reported in Ref. 1. Nevertheless a red shift slightly larger in the case of As than for P (by about 10 meV for $N_i = 2 \times 10^{21}$ cm^{-3}) seems to have been observed. This difference in shifts agrees with pseudopotential calculations based on the virtual crystal band structure of Si-P and Si-As alloys. The main shift (0.3 eV) is interpreted in terms of the self-energy (real plus imaginary parts) of the band electrons in the presence of the impurities. At low absorption coefficients ($\alpha < 10^5$ cm^{-1}) an enhancement of the absorption produced by As doping as compared with similar P doped samples, suggest a greater effectiveness of As in inducing zero phonon indirect transitions.

The samples were 10 x 10 cm (100) oriented 0.765 μm thick commercial SOS films manufactured by Union Carbide.[2] The sample thickness was determined from the optical interference fringes found in the transmission spectra using the refractive index of Ref. 3. The samples were ion implanted with As doses of 5×10^{16} cm^{-2} (sample Si(AsI)) and 2×10^{16} cm^{-2} (Si(AsII)) at 350 keV and with a P dose of 5×10^{16} cm^{-2} at 190 keV (Si(P)). After implantation, the samples were annealed with 10 nsec 0.9 Joule/cm^{-2} pulses of an excimer laser (XeCl, λ = 308 nm). Carrier densities in the implanted layer were obtained via infrared reflectivity. We have used the location of the reflectivity minimum together with the experimental results for bulk samples tabulated by Fistul[4] and the recent study by Migao[5] et al. on ion implanted Si. The carrier concentrations obtained in this way (7.3×10^{20} cm^{-3} for Si(AsI), 4.6×10^{20} cm^{-3} for Si(AsII), and 7.4×10^{20} cm^{-3} for Si(P)) were found to be somewhat smaller than those obtained from the implantation

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dose and the thickness of the implanted layer measured for similarly prepared films on Si (0.265 μm). The reason for the low doping efficiency can be either a precipitation of part of the dopant or a partial compensation by acceptor levels such as, for instance, vacancies.

The absorption spectra were measured at room temperature with a CARY 17D double-beam spectrometer. It was assumed, in the processing of the data, that the samples were composed of two films, one heavily doped of thickness d = 0.265 μm and another one unimplanted of thickness D = 0.500 μm. The thickness of the doped layer was set at 0.265 μm by comparison with that observed for implantation on bulk silicon. It agrees with that expected from the projected range (∿0.15 μm) plus a spread of ∿0.1 μm for the laser annealing process.

We show in Figure 1 the absorption spectrum measured for an unimplanted, unannealed sample as compared with transmission data obtained for similar samples by Hulthén[3] and for mechanically ground and polished films by Dash and Newman.[6] The agreement between the data of Hulthén and ours is excellent. The data of Ref. 6 fall somewhat lower, a fact which is probably due to lattice mismatch strains in the SOS samples.[7] We have also plotted in this figure the data of Aspnes and Studna[8] obtained mainly by ellipsometric techniques. In view of the shortcomings of these techniques, the agreement is to be regarded as good.

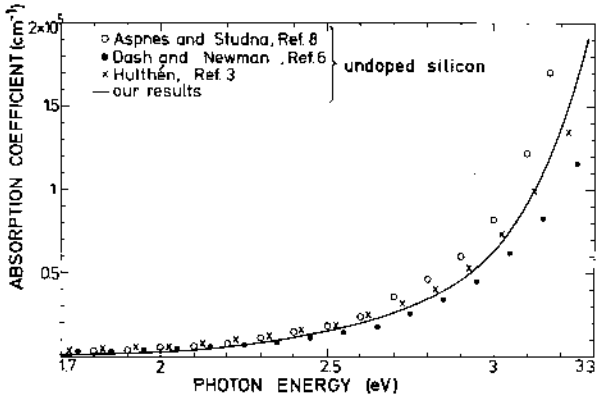

Fig. 1: Absorption spectra of pure silicon as measured for SOS samples at room temperature, compared with the data of Refs. 3-5.

We present in Fig. 2 our data for the unimplanted (pure) sample as compared with our results for the 3 doped samples together with the data of Ref. 1 for $N_i(As) = 4.6 \times 10^{20}$ cm^{-3}. These data show clearly that the ellipsometric results of Ref. 1 must be in error. It has been recently suggested by Aspnes et al.[9] that this error is likely to arise from surface roughness in the As-implanted samples. An indication of the spurious nature of the absorption reported in Fig. 1 has also been obtained by means of ellipsometric measurements on bulk samples, presumably less rough than implanted films.[10]

The behavior observed for the absorption spectra of our implanted samples (Fig. 2) can be described as follows. The red shift of 0.3 eV observed at high absorption (2×10^5 cm^{-1}) for the most heavily implanted samples (Si(AsI), Si(P)) can be explained as the effect of the screened impurity potentials on the E_1 energy gap of silicon (3.38 eV at room temperature).[9-12] This gap shifts down by about 0.15 eV at doping levels of 2×10^{21} cm^{-3}.[10-12] It also broadens by about 0.11 eV. Since $\alpha \simeq 10^6$ cm^{-1} at the E_1 gap[8], the data of Figs. 1 and 2, for $\alpha \simeq 2 \times 10^5$ cm^{-1}, correspond to the lower tail of the gap. They would be expected to shift by the shift plus twice the broadening of the E_1 energy (real plus twice the imaginary parts of the self-energy), i.e., by ∿0.37 eV, in rather good agreement with our results. The data for the Si(AsII) sample suggest a sublinear variation of these self-energies on impurity concentration. This would agree with theoretical and experimental results which yield self-energies proportional to $N_i^{0.5}$.[10-12]

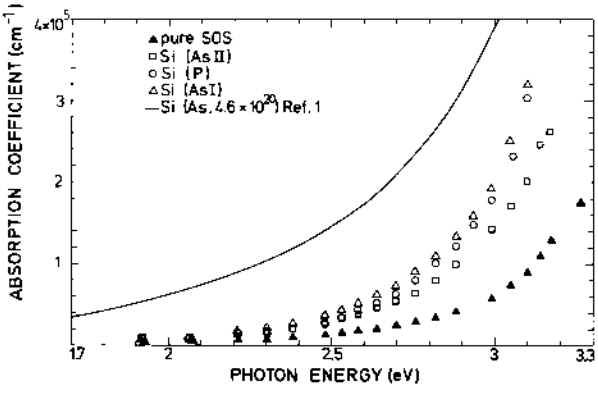

Fig. 2: Absorption spectra measured for SOS samples Si(AsI), Si(AsII), SiP, and pure Si at room temperature, compared with the data of Ref. 1 for an As-doped sample with $N_i = 4.6 \times 10^{20}$ cm^{-3}.

Figure 2 shows that the red shift of the gap is ∿25 meV larger for Si(AsI) than for Si(P) although both samples have the same implantation dose and nearly the same free electron concentration. This difference is, however, small and should be checked more carefully. We have performed pseudopotential calculations of the virtual crystal band structure of Si(P) and Si(As) alloys using for P, As, and Si pseudopotential form factors from Ref. 13. We find for the Si(P) alloys the same E_1 gap as for pure Si, while the gap of the Si(AsI) alloy is red shifted by 32 meV, in excellent agreement with our results.

The stronger perturbation produced by the As atoms, with respect to P, also seems to manifest itself in the low absorption tail ($\alpha < 10^5$ cm^{-1}) of Fig. 2. This tail is probably due to impurity induced indirect transitions. For the same dopant concentration they are stronger in the case of As than for P.

We would also like to mention that Sood[14] has recently estimated the absorption coefficients of samples Si(P) and Si(AsI) at 2.41 eV from the width of the Brillouin lines. He finds $\alpha \leq 5 \times 10^4$ cm^{-1} which agrees with the results reported here.

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