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Energy Levels and Negative Photoconductivity in Cobalt-Doped Silicon*

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Some effects of cobalt doping on *n*-type silicon have been studied. Two deep acceptor levels have been found; the upper one 0.53 eV from the conduction band and the lower one 0.35 eV from the valence band. This double-acceptor behavior leads to extrinsic negative photoconductivity. The spectral response, frequency response, and temperature dependence of this negative photoconductivity are reported.

INTRODUCTION

COBALT in silicon has previously been found to cause deep-level positive resistance oscillations[1,2] and extrinsic photoconductivity.[1] We have found that Co also causes negative extrinsic photoconductivity, and believe that this is the first report of such an effect in Si. We have studied the nature and position of the deep levels introduced by the Co impurities by measurements of resistivity versus temperature, Hall effect, and photoconductivity. Cobalt acceptor levels have been found at 0.35 eV above the valence-band edge and 0.53 eV below the conduction-band edge.

SAMPLE PREPARATION

Wafers of high-purity Si, both *n* type and *p* type with resistivities of 5 to 150 Ω cm were chemically cleaned and Co was evaporated on both surfaces from a tungsten filament. The wafers were then sealed in quartz ampoules with an argon backfill, diffused at various temperatures for a time sufficient to give a uniform cobalt distribution (e.g., 18 h at 1100°C), and then quenched in water. The wafers were then either etched or polished to a thickness of 0.010 in. or less and samples for both Hall-effect and resistivity measurements, and for negative photoconductivity were cleaved from them. For resistivity and Hall-effect measurements, samples were contacted with four small Au+1% Sb dots around their perimeter in the van der Pauw configuration.[3] For the negative photoconductivity measurements the samples were in the form of long bars and were alloyed at both ends to ceramic discs metalized with Au-Sb. The distance between contacts on these discs is 0.5 mm while the area of the sample on which light was incident was about 3×10^{-3} sq. cm.

NEGATIVE PHOTOCONDUCTIVITY

If extrinsic light is shined on a sample of Co-compensated *n*-type Si at room temperature, and the light is chopped, one finds (in many samples[4]) a photoconductive signal as illustrated in Fig. 1 and as described below. Although the response time is faster in Si, the shape of the curve is quite similar to that previously observed for negative photoconductivity in Ge containing certain deep impurity levels.[5,6] This suggests the possibility that the same general model proposed by Stockmann[5] and by Johnson and Levinstein[6] for Ge may also be applicable to negative photoconductivity in Co-doped Si. This model is illustrated in Figs. 1 and 2. When the light is turned on, electrons are excited from the valence band to an upper impurity level which is not completely filled with electrons (1) thus leaving a hole to give some positive photoconductivity (2). The hole rapidly recombines at a lower impurity level which is normally filled with electrons (3),[7] and an electron from the conduction band is then trapped at the lower level (4) thus decreasing the conductivity below the dark level (time constant ~4 msec). When the light is turned off, holes are no longer created in the valence band, thus further decreasing the conductivity (5), but electrons are then slowly

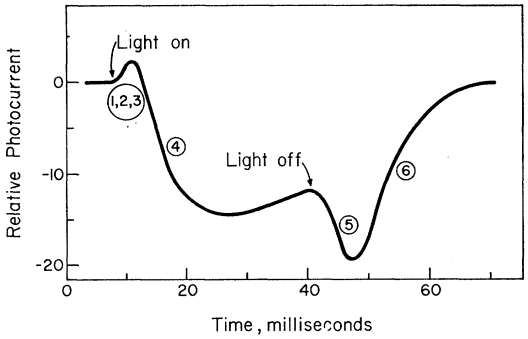

FIG. 1. Negative photoconductivity with chopped extrinsic light in Co-compensated *n*-type Si at room temperature.

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[2] J. S. Moore, Claude M. Penchina, N. Holonyak, Jr., M. D. Sirkis, and T. Yamada (to be published).

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[4] The samples were originally 5 to 10 Ω cm *n*-type Si and were compensated with Co to 4000 to 50 000 Ω cm.

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[7] The slow rise in positive photoconductivity is due mainly to the shape of the light pulse.

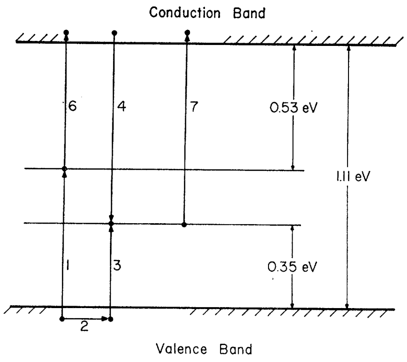

FIG. 2. Energy-level diagram and transitions involved in negative photoconductivity of Co-compensated *n*-type Si.

(time constant ~6 msec) ionized thermally from the upper level to the conduction band (6), thus increasing the conductivity back to the dark level. At increased photon energy (but still extrinsic) one expects to find an additional positive photoconductivity due to direct excitation of electrons from the lower impurity level to the conduction band (7).

As a first check of this model, a study has been made of the spectral response of negative photoconductivity with light chopping rate as a variable. We have employed phase sensitive amplification, locked-in to a variable-speed chopper and adjusted in phase for a positive photosignal with intrinsic light. The resulting photoresponse normalized to a constant photon flux is shown in Fig. 3.

As expected from Fig. 1, a high chopping rate decreases the negative contribution to the photosignal at low photon energies. At higher photon energies the net photosignal goes positive at the higher chopping rates, indicating that an additional process for positive photoconductivity takes place. This is the direct excitation of electrons from the lower impurity level as predicted in the model (process 7).

As seen at slow chopping speeds the negative photosignal begins at a threshold photo energy of 0.59±0.02 eV and increases at higher energies. The rate of growth of negative photoconductivity decreases markedly above 0.76±0.02 eV. Thus the photoresponse seems to be in rather good agreement with the above model and indicates that the energy of the upper level is 0.59 eV above the valence band edge and the energy of the lower level is 0.76 eV below the conduction band edge.

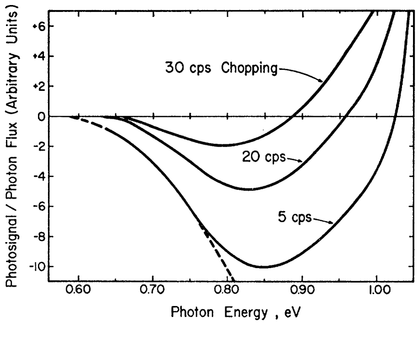

FIG. 3. Photoconductive spectral response of Co-compensated *n*-type Si at room temperature, with various light chopping rates.

The negative photosignal is quite strongly temperature-dependent. For example, the most sensitive sample (at room temperature) has its best response in the temperature range of 14 to 18°C. By 50°C the negative photosignal essentially vanishes owing to the increased rate of thermal ionization of electrons from the upper level to the conduction band. At the other extreme, by 0°C the photosignal becomes positive. This is explained by the continued production of holes in the valence band, while the number of conduction electrons available to be trapped decreases drastically. Figure 4 is the spectral response of this positive photosignal at −37°C (plotted on a log-log scale) showing a threshold energy of 0.58±0.02 eV and a rise from threshold as the $\frac{3}{2}$ power of the energy difference (possibly indicating a forbidden transition).[8]

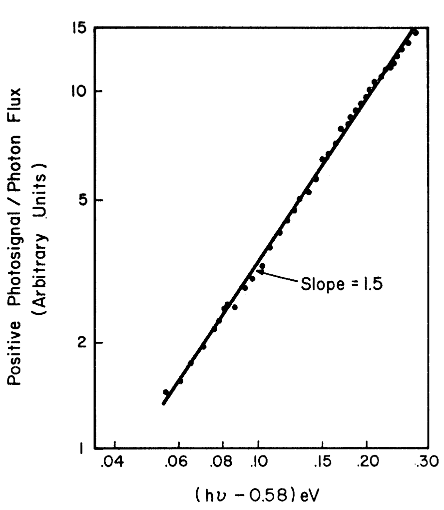

FIG. 4. Photoconductive spectral response of Co-compensated *n*-type Si at −37°C.

The strong dependence of the negative photosignal on conduction electron concentration and thermal ionization rate from the upper level leads us to believe that negative photoconductivity would be observed in *n*-type Si with various degrees of Co compensation, as long as the proper operating temperature is chosen.

RESISTIVITY MEASUREMENTS

In *p*-type Si samples diffused with Co we have found no evidence of any compensation. This implies that the Co levels we have identified act as acceptors and that Co does not introduce donor-like deep levels in Si.

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[8] J. Bardeen, F. J. Blatt, and L. H. Hall, *Photoconductivity Conference* (John Wiley & Sons, Inc., New York, 1956).

As an independent check of the position of the upper Co energy level, the resistivity of several Co-compensated *n*-type samples has been measured. For these measurements samples were chosen which had resistivities of 7, 8, and 22 Ω cm before compensation and less than 20 000 Ω cm after compensation. Hall mobilities of these samples were greater than 1000 cm^2/volt sec after compensation. These measurements indicate a zero-temperature thermal ionization energy[9] from the upper Co level to the conduction band of 0.55±0.02 eV.

DISCUSSION OF ENERGY LEVELS

We have obtained three independent measurements of the energy of the upper Co level in Si, two with respect to the valence band edge, one with respect to the conduction band edge. As the measurements have been performed at different temperatures, and the energy gap of Si varies with temperature,[10] we have adjusted all values to room temperature assuming that the impurity level changes in proportion with the energy gap. Based on a room temperature gap of 1.11 eV,[10] we find the position of the upper Co acceptor level below the conduction band to be 0.52±0.02 eV from negative photoconductivity; 0.54±0.02 eV from positive photoconductivity; and 0.53±0.02 eV from resistivity versus temperature

For the lower Co acceptor level at room temperature an energy of 0.35±0.02 eV from the valence-band edge is indicated from negative photoconductivity measurements.

SUMMARY AND CONCLUSIONS

We have demonstrated that Co introduces two deep acceptor levels in Si, and moreover produces negative photoconductivity consistent with the model proposed by Stockmann[5] and by Johnson and Levinstein[6] for similar effects in Ge. The two acceptor levels are found to be 0.35±0.02 eV above the top of the valence band, and 0.53±0.02 eV below the bottom of the conduction band, respectively.

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Influence of Uniaxial Stress on the Indirect Absorption Edge in Silicon and Germanium

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The indirect optical absorption edge in silicon and germanium has been studied in the presence of shear strain. The splitting observed in the transmission spectrum is dependent on the direction and magnitude of the applied stress and on the polarization of the light with respect to the stress axis. The results have been interpreted in terms of changes in the valence- and conduction-band structure with strain. Neglecting strain dependence of phonon energies, various deformation potential constants have been determined from the experiments. The values are: Si, 80°K: $\Xi_u=8.6\pm0.2$ eV, $|b|=2.4\pm0.2$ eV, $|d|=5.3\pm0.4$ eV, $\Xi_d+\frac{1}{3}\Xi_u-a=3.8\pm0.5$ eV. Si, 295°K: $\Xi_u=9.2\pm0.3$ eV, $|b|=2.2\pm0.3$ eV, $\Xi_d+\frac{1}{3}\Xi_u-a=3.1\pm0.5$ eV. Ge, 80°K: $\Xi_u=16.2\pm0.4$ eV, $b=-1.8\pm0.3$ eV, $d=-3.7\pm0.4$ eV, $\Xi_d+\frac{1}{3}\Xi_u-a=-2.0\pm0.5$ eV. An observed nonlinear dependence of the splitting on stress has been interpreted as shifts of the exciton energies with uniaxial stress. A special experimental technique using a vibrating slit in the spectrometer was used in order to obtain an accurate determination of the fine structure in the absorption spectrum.

1. INTRODUCTION

In the presence of shear strain in a cubic semiconductor the reduced degree of symmetry gives rise to significant changes in the band structure. Based on group theory and $\mathbf{k}\cdot\mathbf{p}$ perturbation calculations, several theoretical investigations[1–5] have been carried out on the valence and conduction bands in Si and Ge.

Thus, the effect of shear strain on the degenerate valence-band edge is found to be a lifting of the degeneracy at $\mathbf{k}=0$. The constant-energy surfaces being "warped" or "fluted" in the unstrained crystal develop into ellipsoidal forms. This behavior can be described by introduction of the deformation potentials *a*, *b*, and *d* defined by Pikus and Bir.[3]

For the conduction-band minima off the center of the Brillouin zone the shapes of the energy surfaces are unchanged to the first order in stress whereas the extremum energy of a particular valley will depend on

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