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PHYSICAL REVIEW B VOLUME 4, NUMBER 4 15 AUGUST 1971

Excited Impurity States and Transient Photoconductivity in Cobalt-Doped Silicon†

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(Received 10 February 1971)

We have studied extrinsic optical absorption and transient photoconductivity due to the two deep impurity levels that cobalt introduces in silicon. The absorption and photoconductivity spectra show that the acceptor level 0.52 eV below the conduction-band edge and the donor level 0.38 eV above the valence-band edge are two different charge states of the same cobalt center, rather than independent states. The long-wavelength optical absorption spectra and the transient response times of positive and negative photoconductivity can be explained in terms of various excited states of neutral, and of positively charged cobalt centers. These excited states lead to a modification in the kinetics of the previously proposed two-level model of negative photoconductivity.

I. INTRODUCTION

Cobalt in silicon has previously been found to introduce deep impurity levels which cause light-sensitive oscillatory current instabilities.[1,2] Studies of the effects of infrared light on the oscillations led us to the discovery of negative extrinsic photoconductivity[3] in n-type Co-compensated Si, which was interpreted by a previously proposed model.[3,4] However, the photosignal was sufficiently weak and the samples sufficiently thin that we were unable to observe either the transient response of photoconductivity or the extrinsic optical absorption under monochromatic illumination. Recently,[5] experiments on diffusion of Co in Si have demonstrated the ability of Co to compensate p-type Si and have located the Co impurity levels more accurately. They were found to be a donor 0.38 ± 0.02 eV from the valence band and an acceptor 0.52 ± 0.02 eV from the conduction band.

We report here on more thorough and extensive investigations of the optical properties of this material. Larger samples made possible the study of the extrinsic optical-absorption spectrum, and a signal-averaging computer made possible a study of the spectral response of transient photoconductivity. These optical data confirm the location of the levels as mentioned above[5] and indicate that they are two different charge states of the same center. Also, from photoconductivity measurements, we have evidence of free-carrier capture on excited centers.

II. MEASUREMENTS

Absorption measurements in the 1.1–2.6-μ region were done on a Cary model 14 double monochromator. For longer wavelengths, a Beckman model IR-10 was used.

For photoconductivity measurements, a Spex $\frac{3}{4}$-m grating monochromator was used to illuminate the sample with extrinsic light chopped by a piezoelectric chopper with variable chopping rate. Photoconductivity transient response signals were processed with a computer of average transients (TMC CAT 4606) to increase the signal-to-noise ratio.

III. SAMPLE PREPARATION

Silicon wafers were prepared for diffusion by degreasing in hot trichloroethane, etching in HF $+ HNO_3$, rinsing in HNO_3, and then rinsing in distilled deionized water. They were then chelated in the trisodium salt of ethylenediamine tetracetic acid (EDTA), rinsed again in deionized water, and dried on filter paper. At least an order of magnitude more cobalt than necessary to compensate to the solid solubility limit[6] of 10^{16} cm^{-3} was quickly evaporated on both faces of the wafer, and the cobalt-plated silicon was then sealed in an argon-

filled quartz ampoule and placed in a furnace. After diffusion for a time (several days) sufficient to ensure a uniform cobalt distribution, the ampoules were quenched in water.

Samples used in absorption measurements were ground and polished to about 4 $mm^2 \times 10$ mm long. For photoconductivity measurements, the samples were bar shaped and typically 1 mm thick. Au + 0.6% Sb (Au + 1% Ga) contacts were alloyed to the ends of the n-type (p-type) samples. The areas adjacent to the contacts were lightly sandblasted and the rest of the sample etch polished.

IV. RESULTS AND DISCUSSION

We have studied samples of phosporous-doped silicon with initial room-temperature resistivities from 11 to 14 000 Ω cm which were compensated with cobalt to final room-temperature resistivities from 200 Ω cm n type to $\lesssim 10^4$ Ω cm p type. The optical properties of these samples depend upon the position of the Fermi energy relative to the two deep impurity levels introduced by cobalt compensation: the lower level being a donor 0.38 eV above the valence-band edge; the upper one being an acceptor 0.52 eV below the conduction-band edge. We classify the samples into three types: (i) n-type material with Fermi energy much above the upper cobalt level; (ii) high-resistivity n-type material with Fermi energy no higher than about kT above the upper cobalt level; (iii) p-type material.

Samples of type (i) show no extrinsic structure in the spectra of either optical absorption or photoconductivity between 0.25 and 0.85 eV. They do, however, show a rapid rise in both absorption and photoconductivity just below the band-gap energy; presumably a tail of the intrinsic indirect absorption edge similar to that found in zinc-doped silicon.[7] This tail will be treated as background absorption in the discussion of type (ii) samples and Fig. 5. Samples of type (ii) have the most interesting extrinsic optical and photoconductive properties and are the ones on which we have done the most extensive studies. Samples of type (iii) have extrinsic absorption spectra similar to those of type (ii) but their photoconductivity spectra are less interesting. The following discussion thus deals mainly with samples of type (ii). We refer back to samples of type (i) and type (iii) later.

Samples of type (ii) exhibit extrinsic photoconductivity at a threshold photon energy of 0.59 eV. Between this threshold and 0.73 eV, the transient response of photoconductivity is similar to that shown in Fig. 1(a) and closely resembles that found[3] when white light is shined on the sample through a germanium filter. This response was interpreted according to a previous[4] model.[8] Light excites holes from the upper cobalt impurity level to the valence band, producing positive photoconductivity and

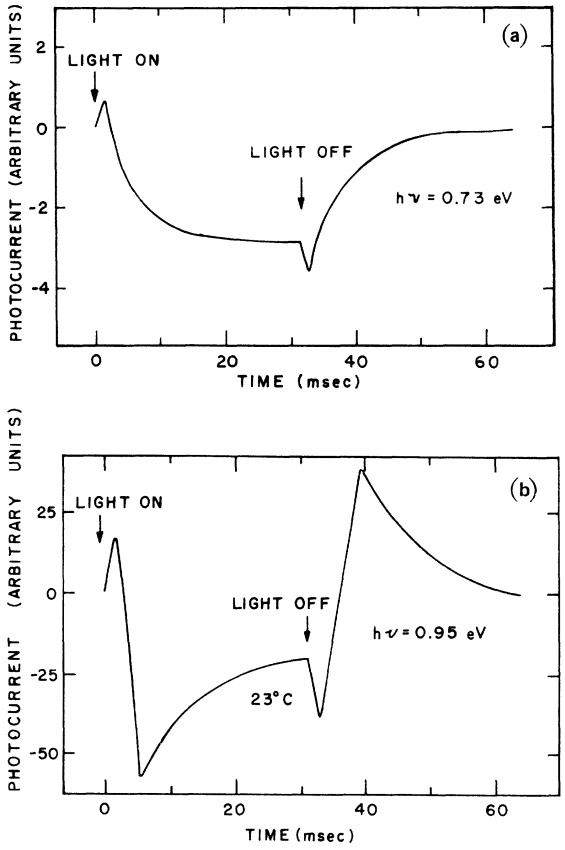

FIG. 1. Extrinsic photoconductive transient response of n-type Co-doped Si (27-Ω cm starting material). (a) $h\nu = 0.73$ eV; (b) $h\nu = 0.95$ eV.

leaving previously neutral acceptor states negatively charged {Figs. 2(A) and 3, processes [1] and [2], respectively}. This hole current very rapidly reaches a steady state; a portion of the holes are trapped on the lower cobalt impurity level, leaving previously neutral donor states positively charged, as shown in Fig. 3, process [3] (the remainder return to the upper cobalt level). Electrons are then taken out of the conduction band when they recombine with holes on the positively charged donors causing negative photoconductivity {Fig. 2(B) and Fig. 3, process [4]} which reaches a steady state as electrons are thermally reexcited to the conduction band from negatively charged acceptors {Fig. 3, process [5]}. When the light is turned off, the hole current rapidly decays causing a further drop in photocurrent. Then, thermal excitation of electrons from negative acceptors returns the current to the dark level. The photoresponse of Fig. 1(a) may thus be thought of as a combination of hole positive photoconductivity [Fig. 2(A)] and electron negative photoconductivity.

At photon energies between 0.73 and 0.99 eV,

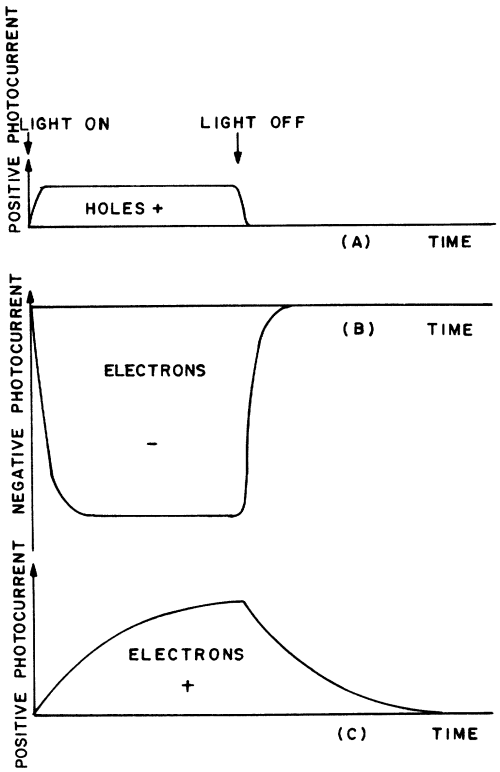

FIG. 2. Proposed photocurrent vs time due to excitation of electrons and holes in our negative photoconductivity model.

an additional slow positive photoconductivity appears and increases with energy as seen from a typical transient response curve at 0.95 eV in Fig. 1(b). This is interpreted as electron current, due to excitation of electrons from neutral donors to the conduction band {Fig. 2(C) and Fig. 3, processes [6] and [7]}. This electron photoconductivity slowly reaches a steady state as electrons recombine with positive donors {Fig. 3, process [8]}. Thus the photoresponse in this energy region is a combination of hole positive photoconductivity [Fig. 2(A)], electron negative photoconductivity [Fig. 2(B)], and

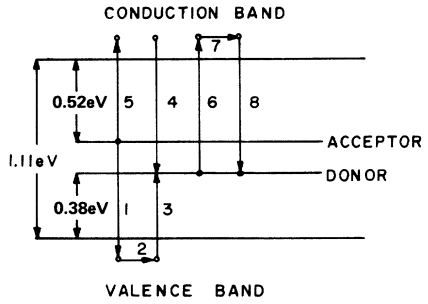

FIG. 3. Energy-level diagram illustrating previous model for photoconductivity in Co-compensated Si.

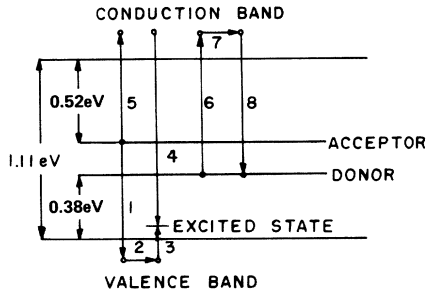

FIG. 4. Energy-level diagram illustrating new model for photoconductivity in Co-compensated Si.

electron positive photoconductivity [Fig. 2(C)].

The fact that the negative photoconductivity is faster (about 3–5-msec time constant at room temperature) than the electron positive photoconductivity (about 7-msec time constant at room temperature) requires a modification of the model previously used to explain negative photoconductivity. In the model as explained above, processes [4] and [8] illustrated in Fig. 3 are identical. This implies that photoexcitation of electrons from neutral donors to the conduction band would simply decrease the negative photoconductivity and would not appear as a separate positive photoconductivity. We can explain the faster time constant for negative photoconductivity if we assume that when photoexcited holes in the valence band are captured by neutral cobalt donors, they do not go directly to the ground state but go instead into excited states,[9] forming excited positively charged cobalt donors. These excited-state holes have larger orbits, and thus have a larger cross section for recombination with electrons than the positively charged donors in their ground state produced by photoexcitation of conduction electrons in the positive photoconductivity. This new model is illustrated in Fig. 4, and we justify it with additional experimental and theoretical arguments below.

The importance of excited states of cobalt impurities to negative photoconductivity was indirectly suggested by experiments to measure the optical absorption cross sections of these impurity centers. The optical absorption by type (ii) samples, as shown in Fig. 5(A), has three noticeable thresholds. One at 0.60 eV corresponds to the threshold for negative photoconductivity (NPC) and one at 0.73 eV corresponds to the threshold for electron positive photoconductivity (PPC). A third threshold, the lowest-energy one, is at 0.52 eV. The dotted line is obtained by subtracting the background absorption [Fig. 5(B)] from the solid curve of Fig. 5(A).

The 0.52-eV absorption threshold might at first be thought (on energy considerations alone) to be due to excitation of electrons from negative cobalt

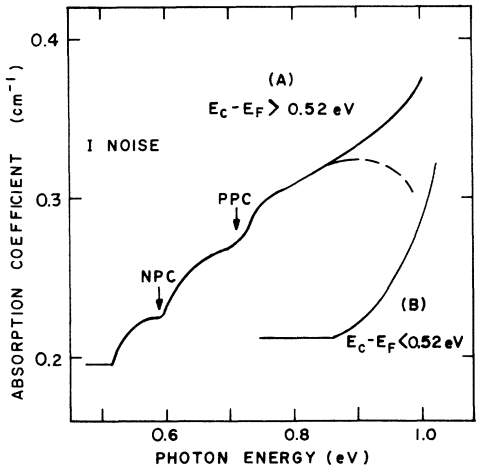

FIG. 5. Optical-absorption coefficient vs photon energy. The Fermi level after cobalt compensation is between the cobalt levels for curve (A) [type (ii) sample, 27 Ω cm n type before compensation], and above the upper cobalt level for curve (B) [type (i) sample, 10 Ω cm before compensation].

acceptors (the upper cobalt level) to the conduction band. However, this would lead to photoconductivity which was never observed at this low threshold energy. Thus, there is no easy optical transition of electrons from negative cobalt acceptors to the conduction band. This "selection rule" is important to the existence of negative photoconductivity, as such a transition would lead to another competitive positive photoconductivity. For example, gold introduces an acceptor level in silicon, 0.54 eV below the conduction band and a donor level 0.35 eV above the valence band.[10] Newman[10] observed positive photoconductivity due to photoexcitation of electrons from the upper (acceptor) level to the conduction band in Si : Au but found no negative photoconductivity, thus illustrating the above discussion. [Just recently, negative photoconductivity has been observed[11,12] in Si : Au at electric fields of the order of 10^5 V/m in the thin-I region of an N^+IN^+ structure (N^+ represents n-type silicon which is highly doped, while I is high-resistivity n-type silicon). Sah and Forbes[12] assume this to be due to the rapid sweep-out of free holes by the applied field. Although this mechanism may be effective in Si : Au, it is not important at the low fields in our bulk samples of Si : Co, see Appendix.]

One might also guess that the 0.52-eV absorption threshold is due to excitation of holes from the ground state of neutral cobalt acceptors (the upper cobalt level) to some unknown impurity states within 0.08 eV of the valence-band edge or excitation of electrons from the neutral donor to some unknown impurity states 0.19 eV from the conduction-band edge. However, the probability of such transitions is rather low owing to the light cobalt doping and the high quality of starting material.

Thus, we can explain the 0.52-eV absorption threshold only as an optical transition from the ground state to a series of excited states (not resolved since measurements were performed at room temperature) of neutral cobalt centers $Co^0 \rightarrow Co^{0*}$. These excited states might be pictured as an electron excited in a large orbit around a positively charged donor center, or as a hole excited in a large orbit around a negatively charged acceptor center. Our experiments cannot distinguish between these two pictures. Although the optical-absorption measurements showed the existence of excited states of cobalt impurities, these excited states could not be the ones involved in negative photoconductivity. This is seen from the fact that there is no photoconductivity (positive or negative) below the 0.60-eV threshold.

Free holes are more easily trapped by negative cobalt acceptors or negative shallow acceptors than by the neutral cobalt acceptors suggested in our model. However, free-hole capture by negative acceptors leads to formation of neutral centers which would not capture free electrons as fast as the positive cobalt donors in electron positive photoconductivity. Hence, (although less frequent than capture of holes by charged acceptors) capture of free holes by neutral cobalt centers (forming excited positive donors) is the important process in a negative photoconductivity that is faster than electron positive photoconductivity. Hole capture by other centers would be a competing mechanism. Thus, we establish our basic model of Fig. 4. We prove it further with measurements as a function of temperature and measurements on samples of type (i) and (iii).

Cooling of the samples below room temperature causes a decrease in the number of free electrons available to be trapped, thus decreasing the negative photoconductivity. At -36 °C this leaves only a small fast positive photoconductivity due to generation of holes {Fig. 4, process [1]} from neutral cobalt acceptors between 0.60 and 0.73 eV (see -36 °C curve of Fig. 6). Heating the sample speeds up the thermal ionization of electrons from negative acceptors {Fig. 4, process [5]} thus speeding up but decreasing the strength of the negative photoconductivity. This is seen from comparison of the 35 and the 23 °C curves in Fig. 6. Above the 0.73-eV threshold, heating or cooling of the sample again decreases the negative photoconductivity, but there it is the slow electron positive photoconductivity which becomes the dominant process (see Fig. 7).

The time constant for negative photoconductivity when the light is turned on (rise time) is considerably faster than when the light is turned off (decay time). This nonlinearity is at first surprising since

the signal level is quite low. However, in equilibrium the concentration of positively charged cobalt centers which are in excited states (Co^{+*}) is very small. Thus the light causes an appreciable change in the concentration of Co^{+*}. Since the capture of electrons by Co^{+*} is what makes the negative photoconductivity faster than the competing electron positive photoconductivity, an increase in the concentration of Co^{+*} due to incident light leads to a decrease in the response time.

The electron positive photoconductivity has essentially the same time constant for rise and decay. This process is linear because the light intensity is too weak to appreciably change the equilibrium concentration of positively charged cobalt centers in the ground state.

Samples of type (i) are n type with the Fermi level much above the upper cobalt level. Thus, there are no holes in this upper level to excite to the valence band, and hence there is no negative photoconductivity and no optical absorption at the 0.52- or the 0.60-eV thresholds [see Fig. 5(B)]. Furthermore, there is no optical absorption threshold at 0.73 eV and no positive photoconductivity at this threshold. This lack of optical transitions from the lower cobalt (donor) level proves that the two cobalt levels are two charge states of the same center. If they had been independent states (e.g., two different complexes of cobalt with other impurities), then the 0.73-eV threshold would be observed whenever the lower cobalt level was filled with electrons, as is the case in both type (i) and type (ii) samples. Instead, for samples of type (i), all the cobalt centers are negatively charged, and there are no neutral centers from which to excite electrons for the 0.73-eV transition; whereas in type (ii) samples the Fermi level is within about kT of the cobalt acceptor level, and a reasonable fraction of cobalt centers is neutral.

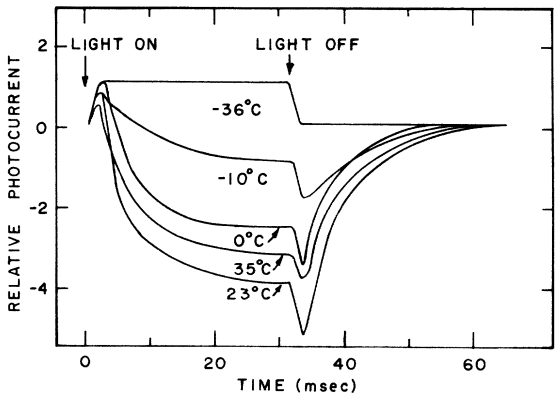

FIG. 6. Extrinsic photoconductive transient response of n-type Co-doped Si (27-Ω cm starting material) at different temperatures for $h\nu = 0.64$ eV. Results are similar for $0.60 < h\nu < 0.73$ eV.

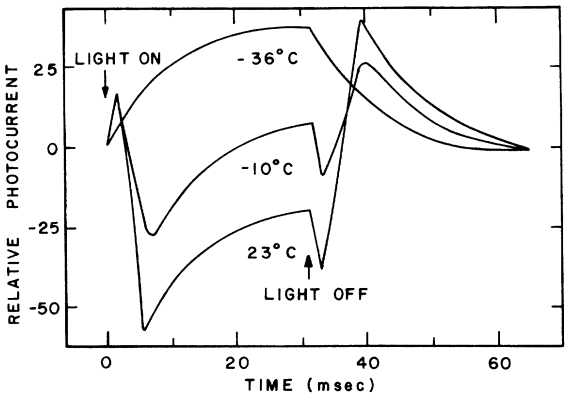

FIG. 7. Extrinsic photoconductive transient response of n-type Co-doped Si (27-Ω cm starting material) at different temperatures for $h\nu = 0.95$ eV. Results are similar for $0.73 < h\nu < 0.95$ eV.

Samples of type (iii) are p type. They do not show negative photoconductivity since there are too few free electrons available to be taken out of the conduction band. They do however show hole positive photoconductivity at the 0.60-eV threshold. The optical-absorption spectrum is similar to that in type (ii) samples.

V. SUMMARY

On the basis of studying transport properties, optical absorption, and photoconductivity data in n- and p-type Si compensated with Co, we have identified that Co has a donor level 0.38 ± 0.02 eV above the valence band, and an acceptor level 0.52 ± 0.02 eV from the conduction band. These are two different charge states of a single Co impurity center. Co impurities also have some excited states in the Si band gap.

Our model for negative photoconductivity is illustrated in Fig. 4. This model is similar to the previous model[4] but requires the capture of conduction electrons by excited holes bound to Co impurities. The model was discussed in terms of the three charge states (+, 0, −) of Co in Si. It can be adapted to other impurities with two deep levels and three charge states (not necessarily +, 0, and −). Negative photoconductivity is observed in Co-doped Si only when the Fermi level is within about kT of the upper Co impurity level.

ACKNOWLEDGMENTS

We wish to acknowledge some useful discussions with C. T. Sah and S. Teitler.

APPENDIX

Sah and Forbes[12] have proposed a new mechanism for negative photoconductivity in strong electric

fields in high-resistivity n-type gold-doped silicon. They neglect the effects of the gold donor level and rely on the electric field to sweep out holes quickly to recombine with electrons at the contacts.

In their gold-doped silicon the rate of capture of conduction electrons by ionized gold donors is a factor of 10^5 slower than the rate of capture of electrons by neutral acceptors. In our samples of Si : Co the rate of capture of conduction electrons by positively charged cobalt donors (Co^+) is roughly of the same order of magnitude as the rate of capture of conduction electrons by neutral cobalt acceptors. The rate of capture of conduction electrons by excited state holes of positively charged cobalt donors (Co^{+*}) is still faster. Thus although it may be reasonable to neglect the effects of the donor level on negative photoconductivity in gold-doped silicon, the donor level is important in cobalt-doped silicon. Furthermore, for the voltages used in our samples (typically 4 – 7.5 V) the transit time of holes across the sample (typically more than 3×10^{-4} sec across 0.8–1.0 cm) is much longer than the time for capture of holes by neutral cobalt donors (estimated as roughly 10^{-7} sec).

Thus, although sweep-cut of holes is the major process to produce negative photoconductivity in gold-doped silicon, capture of holes by neutral cobalt centers is the more effective mechanism in the negative photoconductivity of our cobalt-doped silicon.

In the Sah and Forbes model, as in ours, photoexcitation of electrons from the acceptor to the conduction band is a process which competes with negative photoconductivity. In their model, this competition is seen to require a threshold electric field proportional to the rate of optical generation of conduction electrons from the acceptor level in order to produce negative photoconductivity.

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†Work supported in part by NSF, ARPA, and AFOSR.

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[11]J. R. Barrett and G. C. Gerhard [J. Appl. Phys. 38, 900 (1967)] reported negative photoconductivity in gold-doped silicon. However, Sah and Forbes (Ref. 12) have shown this to be present only in high electric fields.

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