concentration for the systems V-Ti[35] and Mo-Re.[36] When the data are presented in terms of an effective electron-atom ratio, there is an apparent shift in the position of the peak of the curve to a value $N_{eff}$ less than 4.7, probably close to 4.4, for the V-Ti system; and an apparent shift in the peak from 6.4 to 6.6 for the Mo-Re system. The physical significance of this is not clear.

The influence of effective valence on resistivity of some of these transition-metal alloys has already been cited.[15]

## SUMMARY

1. The change in electron-atom ratio $N_{eff}$, which includes a solute size correction to determine an effective valence of the solute in a transition-metal matrix such as niobium, reveals a linear relationship with $T_c$ for dilute alloys of niobium with transition-metal solutes selected from columns 4 through 10 of the periodic table.

2. For transition-metal alloys of columns 4 and 5 and columns 6 and 7, with body-cubic centered structures, the function $T(N_{eff})$ has peak values at approximately 4.4 and 6.6, respectively, whereas the unmodified functions were earlier shown to have average peak values at approximately 4.7 and 6.4.

3. In these transition-metal alloys, the influence of solute size on effective valence and on $T_c$ appears to be independent of whether the solvent or solute are of the 3*d*, 4*d*, or 5*d* series.

4. The concept of effective electron-atom ratio offers a simple means for accounting for maxima in $T_c$-composition curves observed in some transition-metal alloys where both the solvent and solute metal are from the same column of the periodic table.

5. Alloys made from transition metals of columns 4, 5, and 6 with a wide range of solubility appear to show that the upper critical field $H_{c2}$ also has a peak value near $N_{eff}\sim 4.4$.

## ACKNOWLEDGMENTS

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# Photomagnetoelectric Effect in Thin *p*-Type Silicon Crystals

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The photomagnetoelectric (PME) open-circuit voltage has been measured at room temperature for thin *p*-type silicon samples subjected to various surface treatments The effect was found to increase linearly with the magnetic field up to 20 kG, but for all surface treatments showed sublinear behavior with photon flux even at relatively low light intensities. This effect, which was more pronounced at shorter wavelengths, could be attributed to an accumulation layer in the space-charge region of the crystal. Toward longer wavelengths the PME voltage versus light intensity became linear and could be used for calculating an effective surface recombination velocity $S^*$ at the border between the space-charge region and the bulk crystal.

## INTRODUCTION

THE photomagnetoelectric (PME) effect in semiconductors has been measured extensively for Ge,[1–3] InSb,[4] InAs,[5,6] PbS,[7] Bi,[8] Te,[9] and theoretical treatments have been given for the case of nonpenetrating light,[10] exponential absorption profile,[11] nonlinear surface recombination rates,[12] and bulk trapping effects.[13] For silicon there exists only one qualitative measurement,[14] and a short note in which the dependence of the effect on light intensity for one wavelength and one surface treatment have been reported.[15] Since the PME effect is generally considered, in conjunction with the photoconductivity (PC), a powerful tool for the investigation of bulk lifetimes and surface recombi-

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nation velocities in semiconductors, it was of interest to determine whether a PME effect of sufficient size can be measured and applied for the study of the more complex properties of silicon surfaces.

In the present research we have investigated the PME effect in thin sheets of silicon in order to minimize the influence of bulk trapping centers. The effect was measured as a function of magnetic field, light intensity, and incident-light wavelength. Simultaneous measurements of the photoconductivity were performed and the results then compared with theory.

## SAMPLE PREPARATION

Thin slices of 1 mm thickness were cut from zone-levelled *p*-type single crystals of 200-Ω cm resistivity with 300-μsec lifetimes. After being cut to $0.5\times1.5$ cm$^2$ area, the samples were lapped to 0.02 cm thickness and ohmic leads were then attached to the short ends by nickel and copper plating, and soldering with indium metal. The back surface was sanded to achieve high surface recombination velocities and the leads and back surface coated with wax for protection during treatment of the front surface. Since it is known from photoconductivity measurements,[16,17] that widely different recombination velocities may be achieved by different etchants, the following front surface treatments were applied to individual samples: (a) One minute etching $CP_4$. (b) Four minutes boiling in 10% KOH solution. (c) Ten minutes etching at room temperature in HF. (d) Five minutes etching at 40°C in 1% $K_2Cr_2O_7$ solution. All measurements were performed in ambient air, and a slight deterioration of the Si surface with time after etching and variation with ambient humidity was observed. However, after making the measurements in a dehumidified room, sufficient stability was achieved for the duration of both PME and PC measurements for the data reported below to be representative of Si after the specified surface treatment and oxidation of the sample in dry air for a few hours. No attempt was made to determine the influence of oxidizing or reducing atmospheres upon the surface recombination velocities, as reported by Harten.[18]

## MEASUREMENTS

Since Aoki's report[15] indicates that the effect increases nonlinearly at relative low light intensities, the PME open-circuit voltage was measured as a function of photon flux at various light wavelengths rather than as a function of light wavelength for a given light intensity. For this measurement, silicon samples that had been subjected to the four different etching treatments, outlined in Sample Preparation, were placed between the poles of a four-inch Varian electromagnet and were illuminated with chopped light obtained from a 6-cm aperture monochromator, having a tungsten lamp as light source. The light intensity was controlled at each wavelength by interposition of a calibrated neutral-density filter and measuring the maximum light intensity by an Eppley thermopile. The leads of the sample were connected, for the PME measurement, directly to a Tektronix 1121 preamplifier, whose output was connected to an oscilloscope. In each case there was observed a more or less large photovoltage even without magnetic field which could have been caused by end effects, unequal oxidation or illumination of the surface or small impurity gradients throughout the sample. In spite of careful masking of the contacts, these spurious photovoltages could never be eliminated

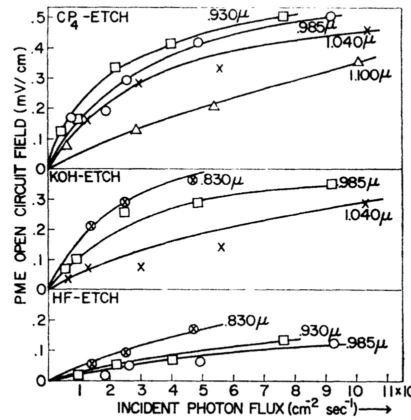


FIG. 1. PME open-circuit field versus incident photon flux for 0.02-cm thin silicon samples at several wavelengths after various surface treatments.

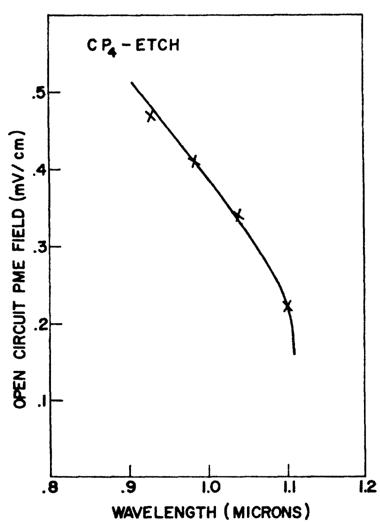


FIG. 2. PME open-circuit field versus wavelength for $CP_4$-etched sample at constant photon flux.

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completely, and had to be subtracted by measuring the PME voltages for both directions of the magnetic field and averaging. The photoconductivity was measured after turning the magnetic field off, connecting the sample by a single switch in series with a comparison resistor and a voltage source, and reading the change in voltage drop across the sample with illumination on the oscilloscope. Again, spurious photovoltaic effects near the contacts were eliminated by reversing the applied voltage and averaging.

## RESULTS

Figures 1(a) through 1(c) plot the PME open-circuit field versus photon flux, taken at 15 kG and various light wavelengths for samples with surfaces that were treated with $CP_4$, KOH, and HF according to the procedure outlined above. $K_2Cr_2O_7$ etching gave essentially the same results as etching by HF and is not plotted further. It is seen that the highest PME effects are obtained for surfaces etched with $CP_4$; the other surface treatments produced qualitatively identical dependence of the PME effect on photon flux. A fairly linear increase of the effect occurs near the absorption edge, but toward shallower absorption the curves become situated increasingly above the longer wavelength curve and assume a more and more sublinear shape.

In Fig. 2 is plotted the PME open-circuit field versus wavelength from Fig. 1(a) at $5\times10^{15}$ photons/cm$^2$ sec. The steady increase of the effect with increasing absorption constant is contrary to the spectral distribution of the PME effect in other semiconducting materials[2,4,7,9] where the response either decreases or remains constant with decreasing wavelength. Figure 3 presents, for comparison, the photoconductivity versus photon flux, measured for the PME sample of Fig. 1(a) only. As expected the photoconductivity shows qualitatively a similar increase with light intensity and wavelength as the PME effect. Figure 4 presents the magnetic-field dependence of $CP_4$-etched samples measured for strong incandescent light pulses and magnetic fields of 20 kG.

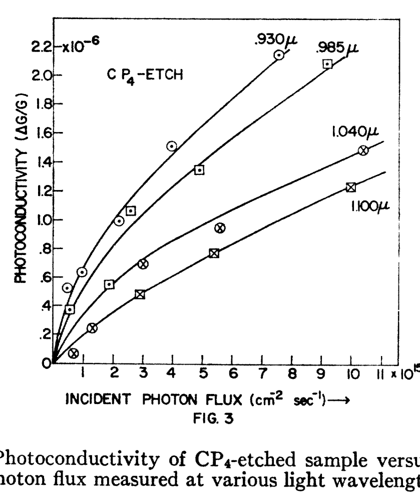


FIG. 3. Photoconductivity of $CP_4$-etched sample versus incident photon flux measured at various light wavelengths.

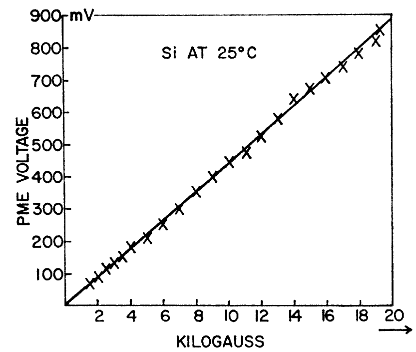


FIG. 4. PME open-circuit voltage versus magnetic-field strength for $p$-type Si at high light intensities. $\rho=200\ \Omega$ cm, $\tau=300\ \mu$ sec.

## DISCUSSION

According to Fig. 4, the linearity of the PME effect in Si extends to higher magnetic field strengths than in Ge,[1] or III-V compounds.[4–6] This is mainly due to the smaller mobility in silicon which permits extension of small-Hall-angle theory to higher field strengths. Under strong illumination it has, therefore, been possible to achieve PME voltages of several volts; these voltages are higher than those normally achieved in other PME materials.

More difficult to explain is the saturation of the PME voltage with increasing photon flux as shown in Fig. 1. Although saturation is predicted for the PME open-circuit voltage by Van Roosbroeck[10] and, for the short circuit current also, by Beatty and Cunningham[12] under their respective cases, neither theory is applicable to our data since in both cases they require the PME field to increase, at small photon flux, independent of wavelength. A different explanation follows from comparison with photoconductivity measurements[16,17] in silicon where surface barriers are believed to cause the nonlinearities of the effect with light intensity. Qualitatively, it is argued, the effect is different for the presence of an accumulation layer than it is for an exhaustion layer. In an accumulation layer, minority carriers drift away from the high-recombination surface in the small-signal case and contribute longer to the current transport than in the "normal" case without surface field. At higher light intensities, the barrier height is decreased and the PC effect approaches the normal case. Conversely, for an exhaustion layer, minority carriers are attracted to the surface and recombine; thus the PC-versus-light-intensity curve lies below the normal curve. At higher light intensities, again, the barrier height is decreased and the curve assumes a superlinear shape.

Our PC-versus-light-intensity measurements plotted in Fig. 3 strongly suggest the presence of such an accumulation barrier in our samples and we suggest that similar considerations may also apply to the PME effect, presented in Fig. 1(a) through 1(c). Minority carrier diffusion is at the shorter wavelengths aided by the space charge field for all our samples. The PME voltage is initially higher than the normal space-charge-free case, that is here sufficiently approximated at the wavelength of penetrating light, and then saturates sublinearly toward higher light intensities. Aoki *et al.*[15] found slightly superlinear increases in the PME and PC effects for Si at nonpenetrating light and concluded from their data the existence of an exhaustion layer, but no experimental proof was presented that their values were actually below the normal barrier-free (penetrating light) case.

The establishment of an applicable PME theory consists in the solution of the equation for electron or hole-diffusion currents:

$$\begin{aligned} i_p(x) &= q(u_p pE - D_p \Delta p), \\ i_n(x) &= q(u_n nE + D_n \Delta n), \\ \mathrm{div}\, i_p &= -\mathrm{div}\, i_n = q\{I(x) - r(x)\}, \end{aligned} \tag{1}$$

where $I(x)=aI_0\exp(-ax)$ is the number of electron hole pairs created at a distance $x$ from the surface, and $r(x)$ the recombination rate throughout the sample. The internal electric field $E$ is established within the crystal due to the separation of movable and stationary electric charges as result of the diffusion process and follows from Poisson's equation

$$\mathrm{div} E = [4\pi/\epsilon k] q(p-n+N). \tag{2}$$

Solution of this system becomes very complex when surface recombination is nonlinear and space-charge effects have to be taken into account. Moreover, it requires exact knowledge of the surface-voltage profile as derived from surface states. Only insufficient information is presently available on silicon surfaces to make this approach fruitful. Instead, we have applied our data for the calculation of the effective surface recombination velocity $S^*$, which describes phenomenologically the combined effect of carrier recombination and surface field in a thin space-charge region on the movement of carriers outside the space-charge region. If we neglect carrier generation in this space-charge region (of $\sim 10^{-4}$ cm) over bulk generation—which is approximately true for our sample thicknesses and the irradiated light wavelength of 1.10 $\mu$—Van Roosbroeck's theory is applicable, and since both the PME field and PC increase at this wavelength almost linearly, can be used to determine $S^*$. From Eq. (49) of Ref. 10 we obtain the following expression for the front-surface recombination velocity if we assume the back-surface recombination velocity to be $>10\,000$ cm/sec:

$$S_f = \theta e R D \rho / E^{\infty} - D/2y_0, \tag{3}$$

where $\theta$ is the Hall angle, $R$ the number of unreflected photons, $E^{\infty}$ the open circuit PME field, $y_0$ the thickness and $\rho$ the resistivity of the slab. $D$ is the ambipolar diffusivity which for an extrinsic $p$-type sample becomes $D_n$, the diffusion constant of electrons in a $p$-type sample.

With the following parameters, valid for $p$-type Si at room temperature and our operating conditions: $\theta=0.24$; $e=1.6\times10^{-19}$ Asec; $\rho=2\times10^2\ \Omega$ cm; D=34 cm$^2$/sec; $y_0=0.02$ cm and the values obtained from Fig. 1 for $E^{\infty}$ and $R=\eta\theta$ for the highest-wavelength curves, together with the assumption of a quantum efficiency $\eta$ of absorbed over incident photons of 0.6 we then obtain for the front-surface recombination velocities after the various surface treatments; $CP_4$ etch: $S=3750$ cm/sec; KOH etch: $S=5170$ cm/sec; and HF etch: $S=12\,200$ cm/sec. These values are compatible with the surface recombination velocities for similar surface treatments obtained from photoelectric measurements by Kontsevoi *et al.*[16] For nonpenetrating light the term "effective surface recombination velocities" is without meaning and $S$ has to be derived by application of diffusion theory in thick space charges similar to those derived by Bir[19] for the special case of linear potential barriers.

## CONCLUSIONS

It has been shown that both the spectral distribution and the light intensity dependence of the PME effect in thin silicon crystals is strongly influenced by space-charge layers at the surface. For nonpenetrating light, the concept of a surface recombination velocity independent of the method of carrier generation is no longer valid, but for penetrating light, the PME and PC method can be applied to determine the effective surface recombination velocities at the border of the space-charge region that describes phenomenologically the combined effect of carrier recombination and surface field within the barrier layer.

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