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Photoelectron paramagnetic resonance of Pt^- in silicon

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The Pt^- center in silicon has been identified by its characteristic electron-paramagnetic-resonance (EPR) signal. From photo-EPR measurements, the optical cross sections of holes for the Pt(0/−) transition have been determined at $T=4.2$ K. A comparison with corresponding optical cross sections obtained for the commonly observed deep acceptor level in Pt-doped Si at $T=80$ K with junction space-charge methods shows that the Pt^- center is, indeed, the impurity which gives rise to the $E_c-0.23$ eV acceptor level.

I. INTRODUCTION

Platinum is known to be a rapid diffuser in silicon and is widely used for different applications in semiconductor technology. In spite of this broad application very little is known about the chemical and structural identity of the centers generated by platinum in silicon. Several Pt-related centers have been observed.[1] Of these a donor level at $E_v+0.32$ eV and an acceptor level at $E_c-0.23$ eV have been extensively studied.[1-8] Although they are often referred to as being directly related to substitutional Pt, the argument for this identification is very indirect and primarily based on the simultaneous appearance of the levels when doping silicon with platinum. Additional arguments often given are the reported thermal stability of the acceptor level at $E_c-0.23$ eV and the comparison with results obtained from EPR measurements. A better understanding of the chemical and structural identity is therefore highly desirable and would be of great importance for the interpretation of recently published data obtained in Si:Pt by Fourier-transform spectroscopy,[9] photoluminescence[10,11] and stress deep-level transient spectroscopy.[7,8]

In the EPR work reported 25 years ago by Ludwig and Woodbury,[12] a Pt spectrum, identified as being Pt^- with spin $S=\frac{1}{2}$, was observed. The structure of the spectrum revealed C_{2v} (orthorhombic) symmetry and the authors interpreted it as arising from a substitutional Pt^- ion distorted from the center in a [001] direction. A different interpretation was later proposed by Henning and Egelmeers,[13] who suggested that the detailed structure of the Pt EPR lines could be explained by assuming that the structure originated from an interaction, including the effect of natural isotope abundance, between a substitutional Pt^- and an interstitial Pt^0. They also observed a lower symmetry (C_{1h}) in dynamical stress experiments using strain-modulated EPR, and concluded that the Pt EPR signal originated from Pt^--Pt^0 pairs where the substitutional Pt^- was distorted in the [001] direction, and the interstitial Pt^0 was responsible for the lower C_{1h} symmetry observed. This result was, however, in disagreement with a general model for the behavior of substitutional transition elements at the end of each series in the periodic table. In this "vacancy" model, which was suggested by Watkins,[14] the Pt^- center is considered as a neutral Pt atom with closed shells, $Pt^0(5d^{10})$, sitting in a negatively charged vacancy V^-. The degeneracy of the partly filled t_2 orbitals of the V^- is lifted by a static Jahn-Teller distortion resulting in a [001] orientation of the defect. Since the agreement between this model and the early EPR results (isolated Pt^-, $S=\frac{1}{2}$, C_{2v} symmetry) was used as a strong argument for the model, Milligan *et al.*[15] performed isotope-doping experiments to investigate whether the alternative interpretation of Henning and Egelmeers was correct. The results from this test showed conclusively that the structure of the EPR lines does not originate from Pt-Pt pairs, thus favoring the original Pt^- model. Furthermore, preliminary static stress experiments showed that the center indeed has C_{2v} symmetry.[15] The microscopic picture of the Pt^- defect seems, therefore, well established.

In junction space-charge measurements the focus has been on the capture process of the Pt-related deep levels, since Pt is known to reduce the lifetime of minority carriers in devices.[1] Depending on the background doping of shallow centers, Pt-related deep levels have been observed close to the conduction or valence band. It seems clear that two of these levels, the $E_c-0.23$ eV acceptor and the $E_v+0.32$ eV donor level, are the only levels that are always present and in appreciable concentrations. The binding energies, optical cross sections, thermal emission rates, and capture cross sections of these levels have been thoroughly investigated,[1-8] resulting in a good understanding of their electronic properties.

Recently, attempts have been made to support the vacancy model by studying the hydrostatic-pressure dependence of the binding energy of the Pt-related deep acceptor and donor levels.[7,8] The Pt acceptor level ($E_c-0.23$ eV) was found to have the same pressure coefficient as the well-known *A* center in silicon. Since the *A* center (an oxygen atom bound to a negatively charged vacancy) is a defect which is believed to be well described by the vacancy model, the observation was considered a strong argument for the applicability of the vacancy model to the Pt^- defect. If the vacancy model is to be used to describe the Pt^- center, the conclusions from these studies are only valid if it can be shown that the Pt-related acceptor level at $E_c-0.23$ eV is identical to the Pt^- center.

Though EPR measurements have provided detailed information on the microscopic structure of the Pt^- center, they have given no information on the energy position of the center in the band gap. On the other hand, the electronic properties of the $E_c-0.23$ eV and the $E_v+0.32$ eV centers have been well characterized by other methods, such as junction space-charge techniques, but these measurements could not give any information on the chemical identity or microscopic structure of the centers.

It is therefore the purpose of this paper to present new data which unambiguously show that the $E_c-0.23$ eV center commonly observed in platinum-doped silicon with junction space-charge techniques is identical to the Pt^- center studied with EPR.

II. EXPERIMENTAL DETAILS

Platinum doping was performed by diffusion of a sputtered Pt film into etched [110]-oriented Si samples. The diffusion, which took place at 1200 °C for 150 h, was performed in Ar-filled quartz ampules. The samples were rapidly quenched in oil, and etched before measurements. Samples of different types (float zone and Czochralsky) and doping (phosphorus and boron doped as well as "undoped") were investigated.

The EPR equipment used is a computer-controlled Bruker ESP 300 spectrometer working in the X band and equipped with an Air Products gas-flow cryostat capable of temperature regulation from room temperature down to liquid-helium temperature. For the photo-EPR[16] measurements, the illumination of the samples was performed using an Applied Photophysics F3.4 grating monochromator. A thermopile detector was used for calibration of the photon flux.

III. RESULTS

All samples showed the characteristic EPR spectrum of Pt^- [denoted $Pt(I)^-$ in Ref. 12], while the high-temperature EPR signal Pt(II), as reported in Ref. 12, was not observed. The details of the Pt^- spectrum (see Fig. 1) are similar to those reported previously.[12,13,15] The spectrum, obtained at 4.2 K with **B**‖[001], shows the central line from the $I=0$ isotopes (^{194}Pt, ^{196}Pt, and ^{198}Pt) and the hyperfine structure from ^{195}Pt with $I=\frac{1}{2}$. The intensity of the hyperfine-structure lines is 34% of the total intensity, which is in good agreement with 33.8%, expected from the natural abundance of ^{195}Pt. The superhyperfine structure from neighboring ^{29}Si atoms is clearly seen and the structure from the, presumably, more distant ^{29}Si atoms is also resolved on the shoulders of the central lines. Furthermore, the g values obtained for the high-symmetry points are in agreement with those previously published (i.e., g_1, g_2, g_3 in Ref. 12).

The EPR signal was always found to be present in darkness for n-type material. In undoped and p-type material, on the other hand, the signal was only observed after illumination. When switching on the light from dark condition, the signal appeared and increased exponentially to a saturation value (see the inset in Fig. 2 which shows the saturated signal minus the signal as a function of time). Upon switching off the light from illuminated condition the signal decreased exponentially to zero. The decay was more rapid when illuminating with $0.5 \text{ eV} < h\nu < 0.8$ eV photons.

The photo-EPR results were obtained by analyzing the initial slope[16,17] of the increasing Pt^- signal at $T=4.2$ K

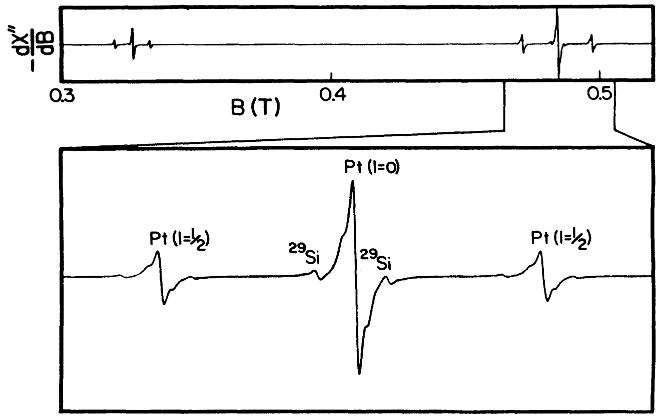

FIG. 1. Derivative EPR spectrum of the Pt^- center in silicon at 4.2 K, **B**‖[001] and $\nu=9.527$ GHz. The lower spectrum, which is part of the total one, shows the central line from the $I=0$ isotopes (i.e., $^{194,196,198}Pt$), the hyperfine interaction of the $I=\frac{1}{2}$ isotope (i.e., ^{195}Pt), and the superhyperfine interaction with ^{29}Si neighbors.

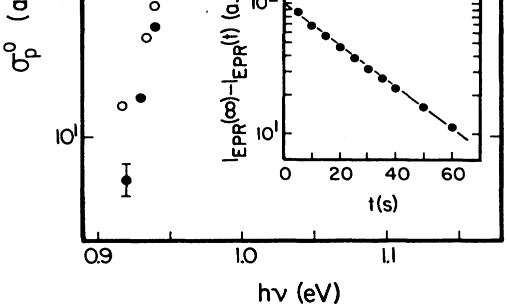

FIG. 2. Optical ionization cross sections for the Pt^- defect, obtained from photo-EPR measurements at 4.2 K (dots). For comparison, corresponding photoionization cross sections for the $E_c-0.23$ eV acceptor level, obtained by Braun, Grimmeiss, and Spann (Ref. 2) using junction space-charge techniques at 80 K (open circles), are also shown. The estimated uncertainty in the photon energy of the photo-EPR spectrum is 2 meV, which is less than the width of the data points. In the inset the saturation value of the photo-EPR signal minus the photo-EPR signal is presented as a function of time for a photon energy of 1.09 eV, showing that the photo-EPR signal transient is a single exponential.

for different photon energies in p-type samples. The initial-slope method could be used only since the photoinduced increase of the Pt$^-$ signal was a single exponential in time (see Fig. 2) for all photon energies, showing that only one defect level was involved in the process. The initial-slope method is faster and increases the spectral range of the measurement. The spectrum, corrected for photon flux, is presented in Fig. 2 and shows the spectral dependence of the ionization cross section σ_p^o for the promotion of a hole from the deep Pt^0 level to the valence band. This interpretation of the measured signal is, however, not obvious and will be explained in detail below.

Due to blackbody radiation of high intensity which was inherently present in our setup, the electronic occupancy of the $E_c-0.23$ eV center decreased very rapidly as soon as the light from the monochromator was switched off. It was therefore not possible to measure the spectral distribution of the ionization cross section for electrons with reasonable accuracy.

IV. DISCUSSION

A comparison of our data with previously published results clearly shows that the EPR signal observed is caused by the Pt$^-$ center. It is then tempting to suggest that the ionization cross section deduced from the observed increase in the Pt$^-$ EPR signal in p-type samples is directly related to the photoionization of the neutral Pt^0 atom, thus giving the optical cross section σ_p^o for the corresponding Pt(0/−) level (Fig. 2). This "obvious" interpretation could, however, be erroneous since the analysis using the initial-slope method could be considerably more complicated because of charge transfer and/or the existence of coupled energy levels. It is therefore necessary to investigate different possibilities which could produce similar data to those presented in Fig. 2 more carefully before reaching a final conclusion.

Let us start by comparing the photo-EPR spectrum with that obtained in junction space-charge measurements. The different optical photoionization cross sections for the two dominating deep levels ($E_c-0.23$ eV and $E_v+0.32$ eV) have been measured[2] at $T=80$ K using photocurrent and photocapacitance techniques. The data for the acceptor level ($E_c-0.23$ eV) have been included in Fig. 2 for comparison, and show a remarkable similarity to the photo-EPR spectrum. The small difference observed between the two spectral distributions at lower energies is due to the different temperatures at which the measurements were performed. The comparison clearly shows that the increase in the Pt$^-$ EPR signal is caused, directly or indirectly, by excitation of holes from the deep $E_c-0.23$ eV acceptor level to the valence band.

If there is only one dominant level in the band gap then the interpretation of the data is trivial, and the result is that the $E_c-0.23$ eV acceptor level is caused by the Pt(0/−) center. However, since it is well established in the literature[1-8] that Pt doping introduces at least two deep levels ($E_c-0.23$ eV and $E_v+0.32$ eV), some other possibilities have to be considered. One such possibility is that the two dominant levels are coupled, i.e., that they are different charge states of the same defect [i.e., Pt(+/0) and Pt (0/−)]. Since the measurements are performed in p-type material, the initial condition in the photo-EPR experiment is Pt$^+$. To reach the Pt$^-$ state, two electrons have to be optically promoted to the Pt center. The kinetic equations describing the photoionization transitions and the capture processes are as follows:

$$\frac{d[\mathrm{Pt}^-]}{dt}=I\sigma_p^{(0/-)}[\mathrm{Pt}^0]-I\sigma_n^{(0/-)}[\mathrm{Pt}^-]-C_p^{(0/-)}p[\mathrm{Pt}^-]+C_n^{(0/-)}n[\mathrm{Pt}^0]\ , \tag{1}$$

$$\begin{aligned}\frac{d[\mathrm{Pt}^0]}{dt}=&I\sigma_p^{(+/0)}[\mathrm{Pt}^+]-I\sigma_n^{(+/0)}[\mathrm{Pt}^0]-I\sigma_p^{(0/-)}[\mathrm{Pt}^0]+I\sigma_n^{(0/-)}[\mathrm{Pt}^-]-C_p^{(+/0)}p[\mathrm{Pt}^0]+C_n^{(+/0)}n[\mathrm{Pt}^+]\\&+C_p^{(0/-)}p[\mathrm{Pt}^-]-C_n^{(0/-)}n[\mathrm{Pt}^0]\ ,\end{aligned} \tag{2}$$

$$\frac{d[\mathrm{Pt}^+]}{dt}=I\sigma_n^{(+/0)}[\mathrm{Pt}^0]-I\sigma_p^{(+/0)}[\mathrm{Pt}^+]+C_p^{(+/0)}p[\mathrm{Pt}^0]-C_n^{(+/0)}n[\mathrm{Pt}^+]\ , \tag{3}$$

$$\frac{dp}{dt}=I\sigma_p^{(+/0)}[\mathrm{Pt}^+]+I\sigma_p^{(0/-)}[\mathrm{Pt}^0]-C_p^{(+/0)}p[\mathrm{Pt}^0]-C_p^{(0/-)}p[\mathrm{Pt}^-]-C_{pn}pn-\sum_i C_{pD}^i pD^i\ , \tag{4}$$

$$\frac{dn}{dt}=I\sigma_n^{(+/0)}[\mathrm{Pt}^0]+I\sigma_n^{(0/-)}[\mathrm{Pt}^-]-C_n^{(+/0)}n[\mathrm{Pt}^+]-C_n^{(0/-)}n[\mathrm{Pt}^-]-C_{pn}pn-\sum_j C_{nA}^j nA^j\ , \tag{5}$$

where I is the light intensity [Pt$^-$], [Pt^0], and [Pt$^+$] are the concentrations of Pt centers in the different charge states, $\sigma_p^{(+/0)},\ldots,\sigma_n^{(0/-)}$ are their optical cross sections for holes and electrons, respectively, and $C_p^{(+/0)},\ldots,C_n^{(0/-)}$ are their capture cross sections. p and n are the concentrations of holes and electrons, C_{pn} the cross section for recombination of holes with electrons, D^i and A^i are trap levels for holes and electrons, respectively, and C_{pD}^i and C_{nA}^j are their capture cross sections. Since we are only analyzing the initial slope of the EPR signal, [Pt$^-$] is very small and we can therefore neglect the terms containing [Pt$^-$]. The absolute photoionization cross sections have been measured with junction space-charge techniques[2] and these measurements show that in the spectral range we are interested in (0.9–1.2 eV), $\sigma_p^{(+/0)}$ is approximately constant and also much larger than the other optical cross sections. If we, e.g., choose $h\nu=1.0$ eV, then $\sigma_p^{(+/0)}\approx 3\times10^{-16}$ cm^2, $\sigma_p^{(0/-)}\approx 2\times10^{-17}$ cm^2, $\sigma_n^{(+/0)}\approx 4\times10^{-18}$ cm^2, and $\sigma_n^{(0/-)}\approx 4\times10^{-17}$ cm^2. This means that in Eqs. (2), (3), and (4) we can neglect all the "optical" terms except the one containing $\sigma_p^{(+/0)}$. In Eq. (5), the only positive term is $I\sigma_n^{(+/0)}[\mathrm{Pt}^0]$. Since $\sigma_n^{(+/0)}$ is much less than $\sigma_p^{(0/-)}$ except for the lowest photon energies, n will be much less than Pt$^-$ and we can neglect the terms containing n. Our kinetic equations will, after these approximations, be as follows:

$$\frac{d[\mathrm{Pt}^-]}{dt} = I\sigma_p^{(0/-)}[\mathrm{Pt}^0] \ , \tag{6}$$

$$\frac{d[\mathrm{Pt}^0]}{dt} = I\sigma_p^{(+/0)}[\mathrm{Pt}^+] - C_p^{(+/0)}p[\mathrm{Pt}^0] \ , \tag{7}$$

$$\frac{d[\mathrm{Pt}^+]}{dt} = -I\sigma_p^{(+/0)}[\mathrm{Pt}^+] + C_p^{(+/0)}p[\mathrm{Pt}^0] \ , \tag{8}$$

$$\frac{dp}{dt} = I\sigma_p^{(+/0)}[\mathrm{Pt}^+] - C_p^{(+/0)}p[\mathrm{Pt}^0] - \sum_i C_{pD}^i p D^i \ , \tag{9}$$

$$\frac{dn}{dt} = I\sigma_n^{(+/0)}[\mathrm{Pt}^0] \ . \tag{10}$$

This analysis shows that the initial slope of [Pt$^-$] will be proportional to $\sigma_p^{(0/-)}[\mathrm{Pt}^0]$. The equation describing [Pt^0], on the other hand, contains only terms which are approximately constant in the investigated spectral range, which means that [Pt^0] is independent of the photon energy and the rise of the Pt$^-$ EPR signal is equal to a constant times $\sigma_p^{(0/-)}$ after corrections for variations in the photon flux. In conclusion, even if the two dominating energy levels are coupled the initial-slope technique should give the spectral distribution of the optical cross section for promoting a hole from the Pt(0/−) level to the valence band.

Another possibility is that the donor level ($E_c+0.32$ eV), coupled or uncoupled, could influence the measured spectrum via two-step photoexcitation of electrons into the conduction band. These photoelectrons could subsequently be captured by the Pt^0 center, thereby increasing the Pt$^-$ EPR signal. However, since the binding energy of the donor level is larger than that of the acceptor level, an increase in the EPR signal should also be observed for photons when $E_g-0.32$ eV $< h\nu < E_g-0.23$ eV. Attempts to observe such signals have failed, thereby excluding this possibility.

A third possibility is that the photoinduced EPR signal is generated by indirect charge transfer via the $E_c-0.23$ eV acceptor level. In this case the acceptor would only act as a channel to promote electrons to the conduction band from which the electrons could be captured by the Pt defect. Since ir illumination increases the speed of quenching of the Pt$^-$ signal, the location of the Pt level has to be in the upper half of the band gap. However, the only level observed in the upper half of the band gap in samples which show the EPR signal is the $E_c-0.23$ eV level,[13] and therefore the Pt$^-$ level and the $E_c-0.23$ eV level have to be identical, which excludes the possibility of indirect charge transfer.

From this analysis it is quite evident that the photo-EPR measurement gives direct information on the optical ionization cross section σ_p^o for the promotion of an electron from the valence band to the neutral Pt^0 center. It is also shown that the photo-EPR spectrum is identical to the σ_p^o spectrum measured for the $E_c-0.23$ eV acceptor level using junction space charge techniques, thereby proving that this deep acceptor is identical to the Pt(0/−) defect observed with EPR.

V. CONCLUSIONS

Photo-EPR measurements on the characteristic Pt$^-$ EPR signal have been performed at $T=4.2$ K. The optical cross section spectrum thus determined was proven to be a direct measure of the ionization of the Pt(0/−) defect. From a comparison with previously published optical cross sections of the two dominating deep levels in Pt-doped silicon (obtained with junction space-charge techniques at $T=80$ K) it is concluded that the Pt defect is identical to the defect giving rise to the $E_c-0.23$ eV acceptor level in Pt-doped Si.

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