

Influence of hydrostatic pressure on the platinum levels in silicon

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Platinum diffusion gives rise to three energy levels in our silicon samples. Deep-level transient spectroscopy detects acceptor levels at $E_c - 235$ meV and $E_c - 500$ meV, and a donor level at $E_v + 320$ meV. The energy shift under hydrostatic pressure for either level was measured for pressures up to 0.50 GPa. The Pt acceptor at $E_c - 235$ meV reveals the same pressure coefficient as was already reported for the well-known A center. This common property supports the recently proposed model of a vacancy-related structure for the substitutional Pt.

Understanding the properties of impurities in semiconductors is essential for understanding the performance of semiconductor devices. Technologically important impurities introduce electrical levels within the band gap.¹ Phenomenologically, impurities are called shallow or deep according to the position of the energy level with respect to the band edges. More precisely, shallow levels are those which can be described by the effective-mass theory (EMT).^{2,3} Because of their small binding energies, these centers determine the conductivity of the samples at room temperature. Deep levels introduce in most cases several electrically active levels within the band gap. The theoretical description, despite the fact that great progress was made recently, still lacks the accuracy and the predictability of the EMT.⁴ Therefore, it is desirable to develop experimentally, criteria for deep levels, which help to classify them. One example was given by Jantsch, Wünstel, Kumagai, and Vogl,⁵ based on the hydrostatic pressure coefficient of the energy levels. The shift of the electronic levels under hydrostatic pressure probes the interaction of the defect wave function with the surrounding host wave functions. Shallow levels have wave functions almost identical to those of the nearby band edge and experience no pressure-induced change of the binding energy. In contrast, deep levels are localized in real space and their wave functions are not exclusively derived from the nearest band. These levels show pronounced shifts in the binding energies under hydrostatic pressure.

Transition metals are typical deep-level defects in silicon. We concentrate in this Rapid Communication on the substitutional element Pt, which is known to introduce several electrically active levels within the band gap.^{1,6-8} The structure of the electron paramagnetic resonance active substitutional Pt⁻ state is well known from the early work of Ludwig and Woodbury.⁹ The $S = \frac{1}{2}$ center is distorted from the T_d symmetrical substitutional site in the [100] direction. Several models have been proposed to explain this behavior. Watkins recently suggested a vacancylike model for the Pt⁻ defect¹⁰ based on the structural similarity between this defect with the A center and the negatively charged vacancy V^- .^{9,11} The creation of a substitutional impurity can be visualized by a two-step process. A vacancy is formed by removing one silicon atom from the lattice site. Afterwards an impurity is introduced and interactions between the vacancy levels and the atomic impurity levels take place. A sufficiently strong interaction forms sp^3 hybrids and shallow impurity levels result. Between the d shell and the vacancy wave functions the interaction is weak. The electrons sup-

plied by the vacancy and the impurity atom first fill the d shell of the impurity and the remaining electrons occupy the vacancy levels. Five electrons occupy these hostlike levels in the Pt⁻ case and give rise to the negatively charged vacancy V^- ($S = \frac{1}{2}$, C_{2v} symmetry). This vacancy model was also recently supported by energy-level calculations of the substitutional Pt impurity¹² and is generally applicable to all substitutional transition elements near the end of each series of the periodic system. This paper is intended to verify experimentally the idea of the vacancy model for platinum.

A 200-Å Pt film was sputtered on the unpolished backside of several different n - and p -type-doped float-zone (FZ) silicon wafers of thickness 0.3 mm. To avoid out-diffusion of the Pt, a silicide was formed by heating the samples for 1 h at 480 °C in a nitrogen atmosphere. Afterwards, the Pt was diffused into the samples at 860 °C for 2 h, again in a nitrogen atmosphere. Control samples without Pt were prepared in the same way. The Pt concentration of these samples was checked by determining the minority-carrier lifetime with a surface photovoltage technique.¹³ The lifetime was reduced to 190 (440) nsec compared to 60 (15) μsec in the n -type (p -type) starting material.

Schottky barriers were formed by evaporating Au onto the polished front side of the wafers on n -type and Ti on p -type material. The shallow doping of the n -type samples was about $(2-3) \times 10^{14}$ phosphorus atoms per cm³ and 1×10^{15} boron atoms per cm³ for the p -type samples as determined by capacitance-voltage measurements.

The measurements of the capacitance transients on the Pt-diffused Schottky diodes were performed with an automatic, computer-controlled system, similar to the one described in Ref. 14. The hydrostatic pressure shift of the various Pt energy levels (up to 0.5 GPa) was determined by using a He gas cell specially designed for low-temperature operation.¹⁵

Two different methods were applied to measure the pressure-induced energy shifts: isothermal transient capacitance measurements (ITC) and deep-level transient spectroscopy¹⁶ (DLTS) measurements. Our experimental setup favors the ITC measurements due to the precisely controllable pressure and temperature. The temperature could be held stable to within 0.05 K to avoid thermal changes of the equilibrium capacity during the measurement of a transient. On the other hand, a DLTS spectrum took about 6 h of cooling time, during which the pressure was held constant to within 1–2%. DLTS spectra were therefore taken only at

zero pressure and at the highest pressure to check the results obtained by the ITC method (zero pressure refers to atmospheric pressure).

The available measurement temperatures for the ITC method are given by the temperature range of the nonvanishing DLTS signal. Compared to the DLTS peak temperature at zero pressure, we used as measuring temperatures at least one lower and one higher temperature within that range. For the smaller temperature, we measured the emission rate up to 1 min, whereas for the higher temperature we measured up to 1 sec but averaged the transients usually 100 times. The energy shifts due to hydrostatic pressure for the lower and higher temperatures are the same. The energy shift due to the hydrostatic pressure, deduced from the DLTS measurements at zero pressure and at the highest pressure, equals the one deduced from ITC measurements within experimental error.

There is agreement in the literature that Pt introduces at least two electrically active levels in the Si band gap. An acceptor level in *n*-type samples with energies varying from $E_c - 230$ meV to $E_c - 260$ meV is reported by various authors.^{1,6} A donor level is found in *p*-type samples with energies varying from $E_v + 320$ meV to $E_v + 360$ meV.^{1,6,7} Some authors detect even deeper levels.⁸

Figures 1 and 2 show typical DLTS spectra of our *p*- and *n*-type samples. The DLTS spectrum without hydrostatic pressure is displayed in the lower part of each figure. The *p*-type samples contain only one dominant peak around 170 K for a concentration of about $3 \times 10^{13} \text{ cm}^{-3}$. We find no Poole-Frenkel shift^{17,18} for different applied electric fields and identify the level according to the literature as the Pt donor level Pt(0/+). The activation energy of $E_v + 320$ meV is deduced from an Arrhenius plot. The *n*-type samples exhibit two dominant DLTS peaks. As shown in Fig.

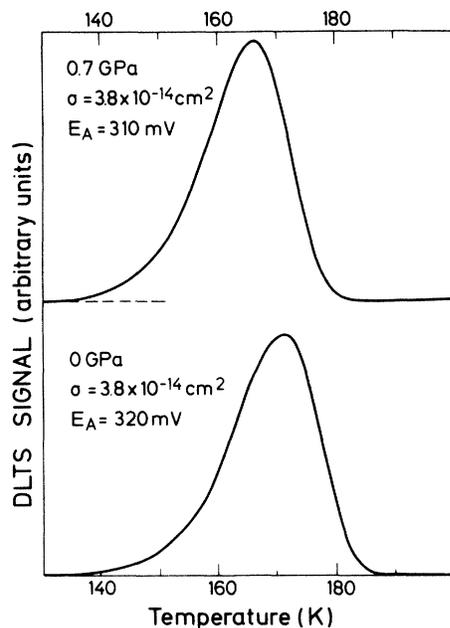


FIG. 1. DLTS spectra of the Pt(0/+) level without hydrostatic pressure in the lower half and for 0.76-GPa hydrostatic pressure in the upper half. Both DLTS spectra ($t_1 = 6$ msec, $t_2 = 7$ msec) can be fitted with the parameters given in the figure.

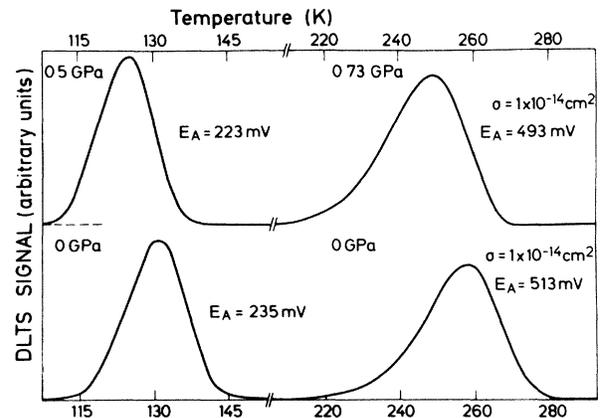


FIG. 2. DLTS spectra drawn in a similar way as for Fig. 1 with the Pt(-/0) acceptor shown on the left side and the Pt correlated center on the right side. The line shapes of the Pt correlated center ($t_1 = 6$ msec, $t_2 = 7$ msec) can be again fitted by the given parameters. In the case of the Pt(-/0) spectra the line shape fits are poor (fits are not shown), and the energetic difference of the levels with and without pressure is therefore deduced from the shift in the peak positions.

2, a low-temperature peak at 120 K and a high-temperature peak at about 260 K are found in these samples. Both levels act as acceptors. The activation energies are $E_c - 235$ meV and $E_c - 500 \pm 20$ meV, the majority-carrier cross sections $5 \times 10^{-15} \text{ cm}^2$ and $1 \times 10^{-14} \text{ cm}^2$, respectively. In the control samples without Pt no deep levels could be detected. Whereas the level at 235 meV corresponds to the well-known Pt acceptor level [Pt(-/0)] the nature of the deeper acceptor level found in all our *n*-type samples is unclear. Brotherton, Bradley, and Bicknell⁶ observe a similar level in their *n*-type FZ samples and attribute it to a gold acceptor level. However, compared with our unpublished DLTS measurements on Au-doped *n*-type samples, we find the level in our Pt-doped sample is not the Au acceptor, although the energetic position is similar to the parameters derived for the Au level. The combination of energetic po-

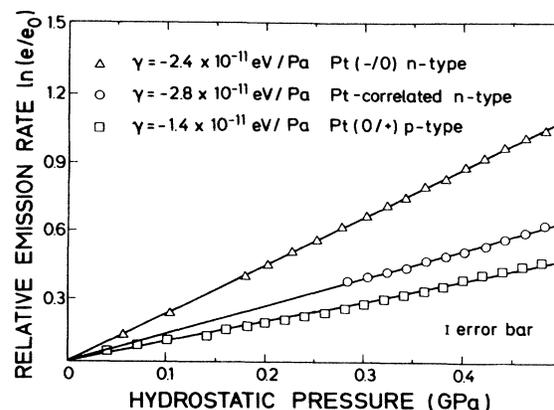


FIG. 3. Dependence of the logarithm of the emission rate upon hydrostatic pressure for the different Pt centers. The curves are linear, and the pressure coefficient γ is deduced from the slopes of these curves multiplied by kT , where k is the Boltzmann constant and T the recording temperature.

TABLE I. Hydrostatic pressure coefficients of the observed levels in DLTS. Additionally, the parameters used to calculate these pressure coefficients are listed for the measured samples.

	Pressure coefficient (10^{-11} eV/Pa)	Activation energy (eV)	Capture cross section (cm^2)	Material
Pt(-/0)	-2.4	0.235	. . .	<i>n</i> -type
Pt correlated	-2.8	0.493	1×10^{-14}	<i>n</i> -type
Pt(0/+)	-1.4	0.320	3.8×10^{-14}	<i>p</i> -type

sition and carrier cross section of the Au level deviates significantly from our level in the *n*-type Pt-doped samples. We believe this level in *n*-type doped samples is Pt associated.

The DLTS linewidth of the low-temperature Pt acceptor is too broad compared with the calculated line shapes in most *n*-type samples. We also find a small shift in the DLTS peak, depending on the sample. By applying different bias voltages, we were able to resolve under certain conditions two DLTS lines, corresponding to two levels separated roughly by 20 meV. We have evidence that both levels belong to the same center, because they show the same hydrostatic pressure dependence. A detailed analysis of the double structure of the Pt acceptor is currently under investigation and will be described in a forthcoming paper.

As was derived by Jantsch, Wüntsel, Kumagai, and Vogl,⁵ the hydrostatic pressure shift γ of the activation energy of the electric levels is given by

$$\gamma = \partial \Delta G / \partial p = kT [\ln e(T, p) - \ln \sigma(T, p)] \quad (1)$$

$\Delta G = E_b - E_t$ is the change in the Gibbs free energy ΔG due to the ionization of the trap. E_b is the corresponding band edge, E_t is the trap ionization energy, $e(T, p)$ is the emission rate which is proportional to the inverse time constant τ of the exponential capacitance transient, and $\sigma(T, p)$ is the capture cross section. The pressure dependence of σ was not determined. However, in similar cases, where the pressure shift of σ was checked, no dependence was reported.^{5,19}

In Fig. 3, the relative change of the emission rates for all three Pt-related levels is plotted versus hydrostatic pressure. The different slopes yield three different pressure coefficients. The results are given in Table I. The accuracy of the pressure coefficients is on the order of $\pm 0.1 \times 10^{-11}$ eV/Pa. The size of the pressure coefficients is similar to the shift of the band gap.⁵ A negative pressure coefficient, as measured for the Pt levels, indicates a reduction in the ionization energy of the electronic level under hydrostatic pressure. In our case, the donor level shifts toward the valence band, and the acceptor level toward the conduction band with pressure. The large pressure shift of the Pt levels proves the deep-level character of the impurity, e.g., the wave function of the Pt^- level is not composed of the nearby conduction-band wave functions. We feel we cannot support the conclusion by Mayo, Lowney, and Bell²⁰ from their photoconductive measurements about the conduction-band-like wave function of this level. The negative pressure

coefficient is consistent with the antibonding character of the Pt^- wave function.

The pressure coefficient of the Pt acceptor level $\text{Pt}(-/0)$ is identical to the acceptor level of the *A* center. The *A* center is a well-known complex of an oxygen atom bound into a vacancy.¹¹ The pressure coefficient of the *A* center was measured by Keller,²¹ and it is also possible to derive a similar value from the uniaxial stress measurements of Meese, Farmer, and Lamp.²² The identical behaviors of the Pt acceptor and the *A* center under hydrostatic pressure can be explained by the vacancy model. In both cases, the bound electron is in an antibonding vacancy state, similar to V^- . No influence of the impurity is expected because the electron is bound to two Si neighbor atoms without any interaction with the impurity.

The second energy level found in *n*-type material shows, compared to the Pt-acceptor [$\text{Pt}(-/0)$] level, a larger energy shift under hydrostatic pressure. As was mentioned already, this level coincides with the energy position of the Au-acceptor level. The Au-acceptor level, as was measured by Nathan and Paul ($\gamma = -1.2 \times 10^{-11}$ eV/Pa)²³ and recently by Li, Chen, Yao, and Bai ($\gamma = -1.9 \times 10^{-11}$ eV/Pa),²⁴ has a much smaller hydrostatic pressure shift. Our own unpublished data on the hydrostatic pressure shift of the Au acceptor confirm the results of Li, Chen, Yao, and Bai. The different pressure coefficient again provides evidence that our level at $E_c - 500 \pm 20$ meV is not the well-known Au level.

In *p*-type Si, the Pt donor level has a pressure coefficient of -1.6×10^{-11} eV/Pa, which is almost identical to the pressure dependence of the band gap²⁵ ($\gamma = -1.5 \times 10^{-11}$ eV/Pa). It seems astonishing that the deep $\text{Pt}(0/+)$ donor level shifts almost parallel to the indirect conduction band with hydrostatic pressure.

We have measured the hydrostatic pressure shift of the Pt levels in silicon. The pressure coefficient of the Pt acceptor ($E_c - 235$ meV) is evidence for the vacancy model proposed by Watkins. Further measurements on the equivalent levels of substitutional Pd, Au, and Ag will show whether the properties of all these elements are determined by the same vacancylike structure.

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