Phonon interactions at the deep platinum acceptor in silicon

M. Kleverman, J. Olajos, and H. G. Grimmeiss
Department of Solid State Physics, University of Lund, Box 118, S-221 00 Lund, Sweden
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High-resolution Fourier spectroscopy has been used to study bound-to-bound transitions at the deep platinum acceptor in silicon. Phonon replicas have been observed for both the $P_{3/2}$ and the $P_{1/2}$ Rydberg series; the energy of the pseudolocalized phonon causing the replicas is 7.2 meV. In addition, Fano resonances associated with the $P_{3/2}$ excited states and their phonon replicas have been observed and analyzed.

INTRODUCTION

In semiconductors impurities with large binding energies have ground states which are more localized than those of shallow centers and are therefore expected to interact more strongly with phonons than impurities with small binding energies.[1] It is therefore not surprising that phonon replicas of optical transitions between ground states and excited states have never been observed for shallow centers in Si, whereas interactions between more localized charge carriers and phonons have often been observed. Recently, several deep impurities have been shown to have excited states which are well described by the effective-mass approximation (EMA). Typical examples of deep centers with EMA-like Rydberg series are the gold acceptor[2,3] and the chalcogen-related double donors[4,5] in silicon with binding energies of the ground state between 200 and 600 meV. No phonon replicas of Rydberg series have been reported for any of these centers although certain electron-phonon interactions in conjunction with Rydberg series of other impurities are known to occur. One example of such an interaction is the broadening of the $1s(A_1)$-$2p_0$ absorption line of Bi (Ref. 6) in silicon which is caused by the coincidence of the excitation energy of this bound-to-bound transition and that of an intervalley optical phonon. Another type of electron-phonon interaction which has been observed for both deep[3,7] and shallow centers[8–10] has been discussed in terms of Fano resonances.[7,9] Such resonance effects occur due to interaction between the final states in the transition: a discrete electron-phonon state and continuum states.

Whereas chalcogens in silicon have been studied in detail, Rydberg series for transition metals had not been reported until recently.[2] Using photothermal ionization spectroscopy (PTIS), both the $P_{3/2}$ and the $P_{1/2}$ Rydberg series have been observed for the gold acceptor in silicon and, in addition, Fano resonances associated with the $P_{3/2}$ excited states have been studied.[3] The relative intensities and the energy differences of the lines observed are very similar to those of group-III acceptors. These results showed that the excited states of the gold acceptor in silicon, in spite of the large ground state binding energy, are well described by EMA.

The purpose of this paper is to present PTIS data for the deep Pt acceptor in silicon which for the first time shows phonon replicas of a $P_{3/2}$ Rydberg series in silicon. We also observe $P_{1/2}$ Rydberg series as well as Fano resonances associated with the $P_{3/2}$ excited states. As for other acceptors in silicon, the phonon participating in the Fano resonances is shown to be the zone-center Γ phonon with an energy of 519 cm^{-1}. Furthermore, three very sharp lines have been observed which are believed to be related, but not directly, to the Pt acceptor.

EXPERIMENTAL DETAILS

Platinum-diffused silicon samples were prepared by sputtering high-purity platinum onto the surface of lapped, polished, and etched ($HF+H_2O$) 14 Ω cm p-type and 200 Ω cm n-type floating-zone silicon. About 1 h sputtering resulted in approximately 100-nm-thick platinum layers. Before diffusion, the quartz ampoule was first evacuated, filled with argon of about 300 mbar, and then sealed off. The samples were then heat treated at 1260 °C for 1–7 d. All samples were quenched to room temperature in diffusion-pump oil giving a cooling rate of about 400 °C/s and after renewed lapping and polishing, some of them were provided with Ohmic contacts by rubbing Ga-Al onto small areas of the surface.

All spectra were obtained with a Bomem DA3 02 FTIR spectrometer. The spectra were divided by an averaged background signal to improve transparency by suppressing slowly varying spectral structures. A liquid-helium continuous-flow Leybold cryostat was used to keep the sample temperature constant at about 10 K.

EXPERIMENTAL RESULTS

A typical PTIS spectrum of our Pt doped samples is shown in Fig. 1. The sharp lines observed are relatively weak and superimposed on a slowly varying background of high intensity in the original spectrum. Only those charge carriers which finally enter a band contribute to the PTIS signal. This implies that some of the bound-to-bound transitions may be (very much) less effective in the production of free charge carriers than other competing optical excitation processes. Therefore, the ma-

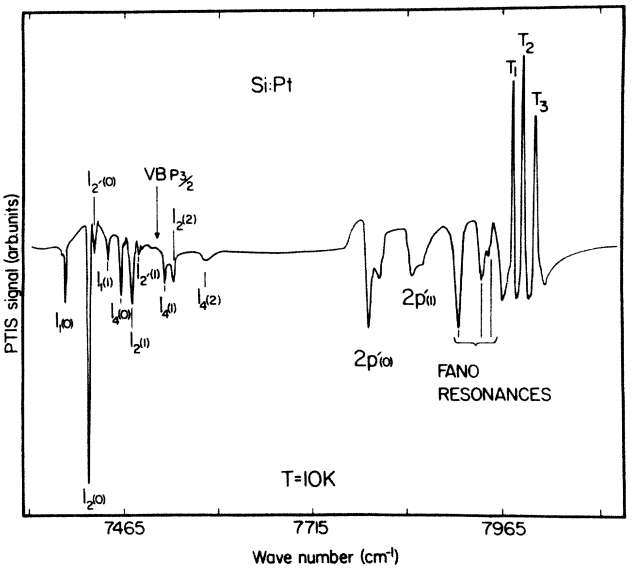

FIG. 1. PTIS measurement of Si:Pt acceptor showing a series of lines due to transitions to excited $P_{3/2}$ states and their phonon replicas at about 7470 cm^{-1}, and excited $P_{1/2}$ states and their phonon replicas at about 7840 cm^{-1}. Fano resonances are observed at about 7920 cm^{-1}. Furthermore, there are three sharp platinum-related lines at 8000 cm^{-1}, yet unassigned.

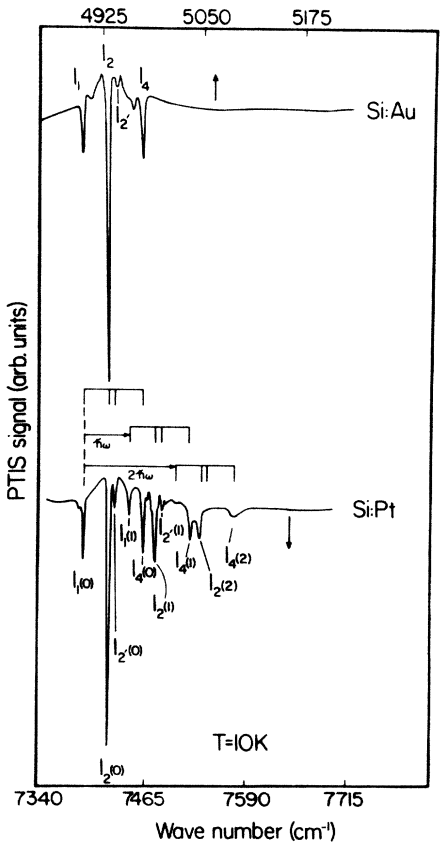

FIG. 2. Comparison of the Si:Au and Si:Pt spectra. To facilitate the assignment of the phonon replicas of Pt, markers indicating 0, 1, and 2 phonon energies (57 cm^{-1}) have been included.

jority of lines in Fig. 1 are observed as negative peaks superimposed on a positive background. Only three narrow lines at about 8000 cm^{-1} which have been labeled T_1, T_2, and T_3 in Fig. 1 gave a positive contribution to the photocurrent.

A group of sharp lines similar to the one previously reported in absorption[2] is observed around 7450 cm^{-1}. In Fig. 2 this part of the Pt spectrum is compared with the $P_{3/2}$ acceptor line spectrum of gold in silicon. It is readily seen that to the series of $P_{3/2}$ gold lines there corresponds a series of Pt lines showing similar energy spacings and relative intensities. These lines of the Pt spectrum are therefore identified as due to hole transitions from the deep Pt ground state to $P_{3/2}$ excited states (see also Table I). We have labeled the lines of the platinum spectrum as $I_m(n)$ where the subindex m is the same as for corresponding lines in the spectra of gold in silicon.[2,3] By n we denote the number of phonons involved as explained further below. The platinum $P_{3/2}$ lines identified above are therefore labeled as $I_1(0)$, $I_2(0)$, and $I_4(0)$ (see Fig. 2). The relative positions and intensities of the $I_m(0)$ Pt lines are also in good agreement with the observed $P_{3/2}$ lines for group-III acceptors.[11] The $P_{3/2}$ valence-band edge VB($P_{3/2}$) is therefore obtained by adding the theoretical binding energy (91.9 cm^{-1}) of the $2P_{5/2}(\Gamma_8)$ state[12] to the observed transition energy $I_2(0)$ giving a value of 7511.1 cm^{-1}.

Figure 2 clearly shows that the group of lines around 7450 cm^{-1} in the platinum spectrum contains more lines than the corresponding spectra for gold (and group-III acceptors) in silicon. These additional lines have been observed in all our samples with the same relative intensities and will now be discussed in more detail. The energy spacings and especially the relative intensities of the $P_{3/2}$ transition lines close to the fourth line in the spectra of the group-III acceptors show a pronounced impurity dependence. Theory[12,13] predicts several excited states close to $I_4(0)$. The appearance of additional lines below VB($P_{3/2}$) in the Pt spectrum could thus be caused by, e.g., a weakening of selection rules governing the spectra of shallow acceptors. Considering that ground states of deep acceptors are not described by EMA, one may speculate that optical transitions from the ground

TABLE I. Observed transition energies of the no-phonon $P_{3/2}$ and $P_{1/2}$ series and for the $P_{3/2}$ Fano resonances of Pt^0. All energies are in cm^{-1}. The energy of the Γ phonon involved in Fano resonances is taken to be 519 cm^{-1}.

Transition	Transition energy	Transition energy $+\Gamma$ phonon	Observed Fano resonance
$I_1(0)$	7388.0	7907.0	7908.9
$I_2(0)$	7419.2	7938.2	7939.3
$I_2'(0)$	7426.1	7945.1	7948.5
$I_4(0$	7462.0	7981.0	
$2p_a'(0)$	7790.6		
$2p_b'(0)$	7802.6		

state to, for example, $nS_{3/2}$ excited hole states may be similarly probable as those to nP states. A weakening of EMA selection rules has indeed been observed for deep donors in silicon which exhibit lines in the spectra not seen for group-V donors. In fact, the intensity of the EMA forbidden $1s(A_1)$-$1s(T_2)$ absorption line of, e.g., S, Se, and Te in silicon is comparable to the intensity of the EMA allowed $1s(A_1)$-np transitions.

However, it is quite evident that deviations from EMA cannot explain all lines in the group around 7450 cm^{-1}, in particular since some of the lines are observed above VB($P_{3/2}$). A close inspection of Fig. 2 shows that the second line [$I_2(0)$] in the Au and Pt spectra has the highest intensity. The energy difference between $I_2(0)$ and the line with the highest intensity among the additional Pt lines [$I_2(1)$] is about 57.5 cm^{-1} (7.3 meV). By repeatedly adding this energy to the Pt $P_{3/2}$ spectrum (which according to Fig. 2 is identical with the Au $P_{3/2}$ spectrum with regard to line spacing and intensities), we obtain a spectrum very similar to the Pt spectrum (Fig. 2). We are thus able to conclude that the additional structure is due to phonon replicas to the Pt $P_{3/2}$ lines. Some of the additional lines close to 7450 cm^{-1} have been observed previously in absorption,[2] but due to the high sensitivity of PTIS were are able to observe several phonon replicas involving up to two phonons, and can accordingly identify the origin of the additional lines.

The phonon giving rise to the replicas is resonant with the acoustic phonon band. Interactions with acoustic-band phonons are relatively weak since the one-phonon replicas have full widths at half maximum which are only about 50% larger than the corresponding no-phonon lines. The phonon involved may therefore be discussed in terms of a pseudolocalized phonon. Using the well-known expression $(S^n/n!)\exp(-S)$ for the relative intensities of the nth phonon replica, the Huang-Rhys factor S is estimated to be 0.4. This value is very small indicating that the coupling to the pseudolocalized phonon is weak and implies a Frank-Condon shift of only about 25 cm^{-1}.

Another source of multiple lines which has to be disregarded is that no-phonon lines can experience isotope shifts.[14,15] Platinum has several stable isotopes whereas gold has only one. The natural abundances of the three main Pt isotopes are about the same. If the observed shifts of the Rydberg series were due to the zero-point vibration of centers involving different platinum isotopes, the three no-phonon $P_{3/2}$ series would be expected to have relative intensities proportional to the natural abundances of the isotopes. Since the observed relative intensities of the three $P_{3/2}$ series are very different we conclude that the additional $P_{3/2}$ series are not caused by an isotope shift of the no-phonon lines.

Figure 1 shows that another structure is observed in the platinum spectrum at about 7800 cm^{-1}. By comparing the platinum spectrum with the gold spectrum (Figs. 2 and 3) it is quite evident that the structure is due to the $2p'$ line of the $P_{1/2}$ series of excited platinum states. It is interesting to note that the energy difference between the $P_{3/2}$ and the $P_{1/2}$ states is not the same for gold and platinum. For platinum the energy difference $2p'(0)-I_2(0)$ is about 371 cm^{-1} (Fig. 1) whereas for gold the difference is 389 cm^{-1}. These two values differ by about 18 cm^{-1} which should be compared with about 8 cm^{-1} for the largest difference observed for group-III acceptors. In Figs. 2 and 3 we arranged the spectra so that the $I_2(0)$ line for gold and platinum coincide in order to facilitate comparison and to show the perfect agreement between the gold $P_{3/2}$ lines and the platinum no-phonon $P_{3/2}$ lines.

About 60 cm^{-1} above the $2p'(0)$ doublet in the platinum spectrum, a similar structure is observed. Since the value of 60 cm^{-1} is very close to that found for the energy shift between the no-phonon and one-phonon $P_{3/2}$ lines, we suggest that this structure is a phonon replica of the $2p'(0)$ lines. As for the $P_{3/2}$ we label the two structures as $2p'(0)$ and $2p'(1)$. Both structures are doublets and the two components have been denoted by $2p'_a$ and $2p'_b$. In Tables I and II the peak values of the $2p'(0)$ and $2p'(1)$ lines have been summarized. The energy difference between the $2p'_a(0)$ and $2p'_b(0)$ lines is about 8 cm^{-1} which is somewhat smaller than the corresponding value of about 11 cm^{-1} for gold. It is quite obvious from Fig. 3 that the relative intensities are very similar for the gold and platinum $2p'_a(0)$ and $2p'_b(0)$ lines and that the same intensity ratio is also found for the corresponding platinum replicas. These results further support our interpretation of our data as being due to a weak interaction between a bound hole and the pseudolocalized phonon. Since the energy splitting and the relative intensities of the $2p'_a$ and $2p'_b$ lines are similar for both gold and platinum, it is reasonable to believe that the splitting of the line is caused for both impurities by the same physical process; however, the exact nature of this phenomenon is not understood at the present.

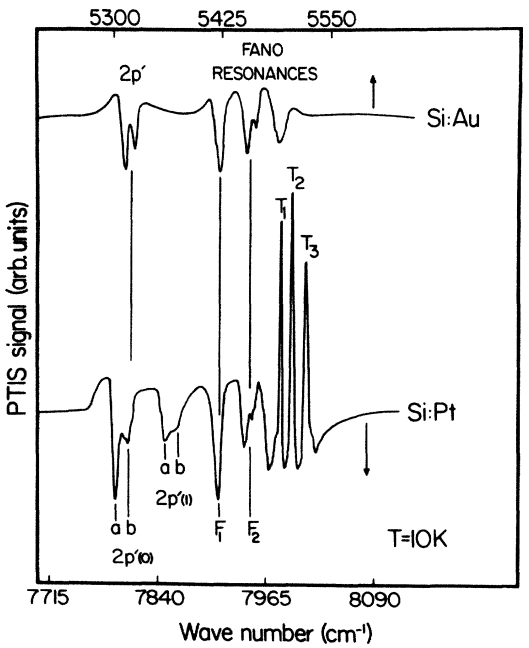

FIG. 3. Comparison of spectra of the Si:Au and Si:Pt $2p'$ transitions and Fano resonances.

TABLE II. Transition energies of the phonon replicas to the no-phonon $P_{3/2}$ and $P_{1/2}$ lines of Pt^0. All energies are in cm^{-1}.

Transition	Transition energy	Energy difference from no-phonon line
$I_1(1)$	7444.4	56.4
$I_2(1)$	7476.4	57.2
$I_2'(1)$	7486.2	60.1
$I_2(2)$	7534.7	115.5
$I_4(2)$	7577.1	115.1
$2p_a'(1)$	7849.4	55.7
$2p_b'(1)$	7858.3	57.8

As for gold in silicon, a weak satellite of the $I_2(0)$ line is observed which has been labeled $I_2'(0)$ (Figs. 1 and 2). The energy difference between the two lines, $I_2'(0)-I_2(0)$, is about 7 cm^{-1} which is close to the difference $2p_b'(0)$-$2p_a'(0)$. A similar satellite is seen for the $I_2(1)$ line which suggests that $I_2'(1)$ is a phonon replica of $I_2'(0)$. The splitting of the $2p'$ line first observed for gold in silicon[3] has previously been discussed; the cause was said to be the lower symmetry of the center than T_d. The final state of the $2p$ transition is believed to be well described by EMA and should therefore transform as a Γ_6 state (a Kramers doublet in T_d symmetry) the degeneracy of which cannot be lifted by a symmetry lowering of the center. The doublet structure of the $2p'$ line may thus originate from a split in the ground state. This interpretation is further supported by the fact that the differences $2p_b'(0)-2p_a'(0)$ and $I_2'(0)-I_2(0)$ are dependent on the impurity involved. More systematic studies on the symmetry of these centers have to be performed for a more definite assignment of the symmetry point group.

Fano resonances, involving $P_{3/2}$ states and the zone-center optical phonon, have been observed for several acceptors in silicon. For platinum we have calculated the energy position of the first two Fano resonances (Table I) by adding the Γ phonon energy (519 cm^{-1}) to the measured transition energies of the $P_{3/2}$ lines. The energies thus obtained are in perfect agreement with the energy positions of two negative peaks F_1 and F_2 in Fig. 3. It is interesting to note that the F_2 Fano resonance shows a similar splitting as the corresponding resonance for gold. The observed splitting for platinum is smaller than for gold but very similar to the differences $I_2'(0)-I_2(0)$ and $2p_b'-2p_a'$ which gives further support to our interpretation of the origin of the $2p'$ doublet. The Fano resonance associated with the $I_4(0)$ line is superimposed on the T_1 line (Fig. 3) and could therefore not be studied.

All our platinum-doped samples, independent of the doping procedure, exhibited three sharp lines of high intensity around 8000 cm^{-1} which we have not been able to see in our gold-doped samples (see Table III). The striking feature of the three lines is that they appear as positive peaks. This may indicate that the lifetime in the band of the free charge carrier due to these transitions is larger than the lifetime of those carriers which are excited from the platinum acceptor. At present we have no explanation for the origin of the three lines.

TABLE III. Transition energies of Pt related lines. All energies are in cm^{-1}.

Transition	Transition energy
T_1	7981.1
T_2	7994.0
T_3	8010.2

DISCUSSION

Although both platinum and gold belong to the $5d$ transition metals and give rise to acceptors with large ground-state binding energies, pronounced differences in their photoconductivity spectra are observed. Apart from the three sharp lines T_1, T_2, and T_3, the platinum-doped samples exhibit replicas of the Rydberg series involving up to two phonons whereas the gold spectra show only no-phonon lines. This indicates that the electron-phonon interaction for platinum, though rather weak, is considerably stronger than for gold. According to the vacancy model,[16] which has previously been proposed for several single substitutional transition-metal impurities in silicon, such as the neutral gold (Au^0) and the negatively charged platinum (Pt^-) centers, both centers correspond to a negatively charged vacancy V^- where either impurity has a filled $5d^{10}$ shell. Whereas two platinum related spectra (Pt I and Pt II) have been detected earlier using electron spin resonance (ESR) (Ref. 17) our samples showed only the Pt I center in ESR (Ref. 18) which is believed to originate from the single substitutional impurity center. In the negatively charged state, ESR shows that Pt I has an unusual dihedral symmetry which is characteristic for V^- in agreement with the above-mentioned vacancy model. The optical-hole transitions studied in this paper take place at neutral centers. According to the vacancy model, Pt^0 resembles the physical properties of V^0 whereas Au^0 resembles those of V^-. It is well known that V^0 is subject to a D_{2d} Jahn-Teller distortion, whereas V^- has a C_{2v} distortion in addition to the D_{2d} distortion of the V^0 center. Whether or not the differences in the proposed point-group symmetries of the centers could affect the electron-phonon coupling is at present unclear.

ACKNOWLEDGMENTS

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