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OPTICAL EXPERIMENTS ON DEEP CENTERS IN SEMICONDUCTORS

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1. Introduction

Crystal defects whose ground states lie in the forbidden energy gap of a semiconductor are often divided into shallow and deep centers. Shallow centers normally lie close to one of the band edges, and their excited states are well described by effective mass theory (EMT) ^{1,2,3)}. The ground states of shallow centers in silicon, for example, have binding energies which are smaller than 100 meV. The assignment of the ground state levels and of the excited states has been considerably facilitated by

the fact that optical absorption spectra of shallow centers generally exhibit detailed structures ⁴⁾. This is one of the reasons for our good understanding of shallow centers in germanium and silicon.

Deep centers have larger binding energies and are caused by both foreign atoms and native defects. In contrast to shallow centers and some transition metal impurities, deep energy levels quite often exhibit smooth photoionization spectra (figure 1). The absence of structured absorption in semiconductors doped with deep impurities has therefore sometimes been explained by the non-existence of excited states for these centers.

In principle, the electronic properties of crystal defects can be studied by both bulk and junction space-charge techniques ⁵⁾. Previous characterization attempts have only utilized bulk techniques, such as Hall measurements, optical absorption, luminescence and photoconductivity. Owing to the high resolution, absorption measurements are often used for studies of electronic structures of crystal defects. Generally, however, it is difficult to obtain absolute values of electronic parameters with bulk techniques.

A break-through in the characterization of deep centers was achieved by the application of different kinds of junction space-charge techniques ^{5,6)}. Junction

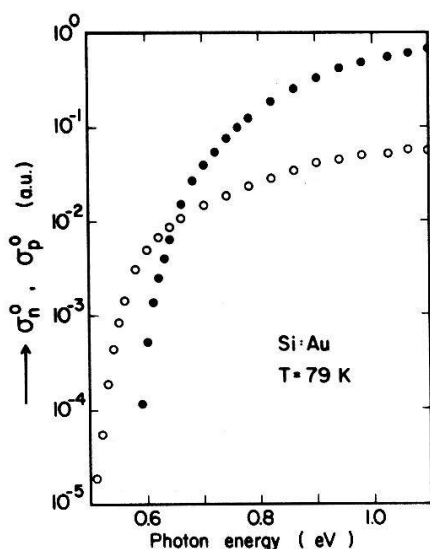


Fig. 1: Optical cross section for electrons and holes versus photon energy for the gold acceptor in silicon ²²⁾ at 79 K.

techniques have the unique ability to yield, from a single sample, information on important electronic parameters of deep energy levels in absolute values.

1962 Krag et al showed ⁷⁾ that sulfur related centers in silicon may exhibit excited states. Recently evidence was given that also selenium and tellurium related centers have excited states ^{8,9,10)}. These measurements made it possible to obtain very accurate information on binding energies of both ground states and excited states ^{11,12)}. The results were obtained from a combination of bulk and junction techniques, which took advantage of both measurement techniques. Using chalcogenide doped silicon as an example, it is the purpose of this paper to show how Fourier spectroscopy applied to both diodes and bulk samples can increase our understanding of the electronic properties of deep centers.

2. Experimental Techniques

The measurement techniques used in this paper are three different methods of Fourier spectroscopy combined with different kinds of junction techniques. Fundamentals of junction measurements in the study of deep energy levels in semiconductors have been described previously ⁵⁾ and will therefore not be further discussed in this paper. Most of the results which are presented in this paper have been obtained by Fourier absorption (ABS), Fourier photoconductivity ¹³⁾ (PC) and Fourier photo-admittance spectroscopy ¹⁴⁾ (FPAS). Whereas Fourier absorption and photoconductivity spectroscopy have been used successfully for many years in the study of crystal defects, Fourier photo-admittance spectroscopy is a new method, which has the high signal-to-noise ratio and resolution of Fourier spectroscopy, as well as the sensitivity of junction techniques ¹⁴⁾.

The spectrometer used in these studies is a Fourier transform IR (FTIR) spectrometer. As in the case of Fourier photoconductivity spectroscopy, the detector is replaced by the sample, which in our FPAS measurements is a diode. As the light intensity varies, an oscillating current is generated in the external circuit of the diode owing to excitation from and capture into localized energy levels within the forbidden energy gap. When a diode is used as "detector" in an FTIR spectrometer, the detector signal is a combination of a large number of such oscillating currents, each current component having a frequency proportional to the energy of the corresponding component of the incident light spectrum. This signal is stored in digital form by the spectrometer's computer, and after a suitable period of data collection, Fourier-transformed into the spectral response of the diode to the known incident spectrum. It has been shown that the alternating current in the external circuit of the diode is proportional to the optical emission rate if transitions only to one of the energy bands

are involved ¹⁴⁾. The experimental conditions can often be arranged so that deviations from linearity between response and emission rates are small.

FPAS has several advantages compared with conventional absorption and junction techniques. Since the light only passes a few microns of material before it becomes active, its intensity is much less affected by phonon absorption than in absorption measurements. It is faster than conventional optical junction techniques, and its resolution capability is considerably better. For levels shallower than 0.2 eV, the method provides the only existing possibility to study the optical properties of deep centers using junction techniques. If very high resolution is not required, any spectrometer with proper modulation of the monochromatic light can be used for these studies.

3. The energy spectrum of substitutional chalcogenide impurities in silicon

Owing to the difference in the valency of silicon and elements from the sixth group of the periodic table, an isolated substitutional chalcogenide impurity in

silicon is expected to form a double donor. If one of the two extra electrons is transferred into an excited state, it will move around a singly charged core. The part of the absorption spectrum which is caused by excited states should therefore be very similar to that observed for the shallow group V donors. The energy spectrum of such a level in a tetrahedral surrounding is shown in figure 2. It should be noted that all states, except the ground state, are shallow states.

Leaving out the s states, the excited states are well described by an effective mass theory (EMT), which takes into account only one conduction band and one conduction band valley ²⁾. However, in order to explain the splittings of the s states, the multivalley nature of the conduction band must be taken into account ^{1,3,4)}.

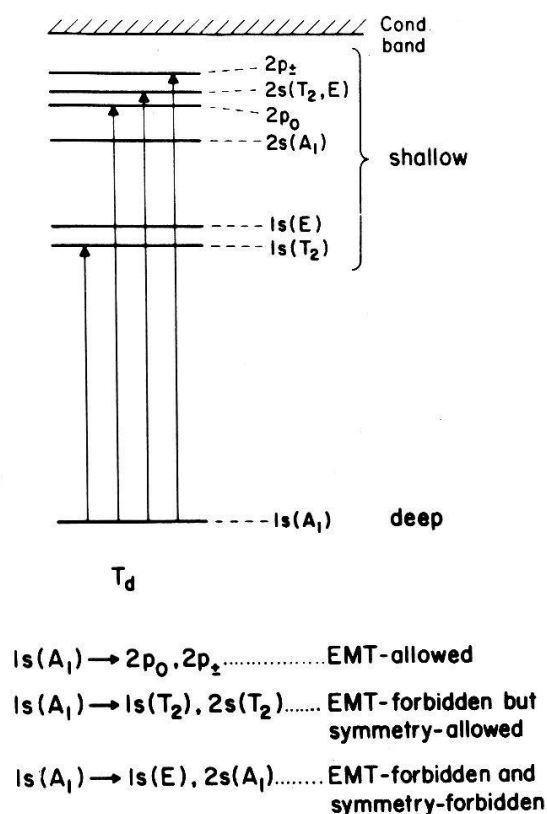


Fig. 2: The lower part of the energy spectrum of a substitutional chalcogenide center in silicon. EMT and symmetry-allowed no-phonon transitions are marked with arrows.

According to EMT, only odd-parity transitions are allowed, for example, between the ground state $1s(A_1)$ and the p states. However, due to the large binding energy of the ground state, symmetry-allowed, but EMT-forbidden transitions are also observed, for example between the $1s(A_1)$ and $1s(T_2)$ states. In figure 2, both EMT and symmetry-allowed transitions between the ground state and excited states are marked with arrows.

Transitions which are both EMT and symmetry-forbidden are not seen in direct optical excitation processes. Accurate values for the binding energy of such states, as for example the $1s(E)$ and the $2s(A_1)$ state, are nevertheless obtainable from absorption measurements if experimental techniques other than direct absorption are utilized in the experiment. It will be shown later that Fano resonances¹⁵⁾ offer one of these possibilities for determining the binding energy of these states. In principle, all existing excited states of an energy level in a semiconductor can be studied with high accuracy using different types of absorption experiments.

4. Experimental results and discussion

Figure 3 shows the Fourier absorption and Fourier photoconductivity spectrum of selenium-doped silicon.

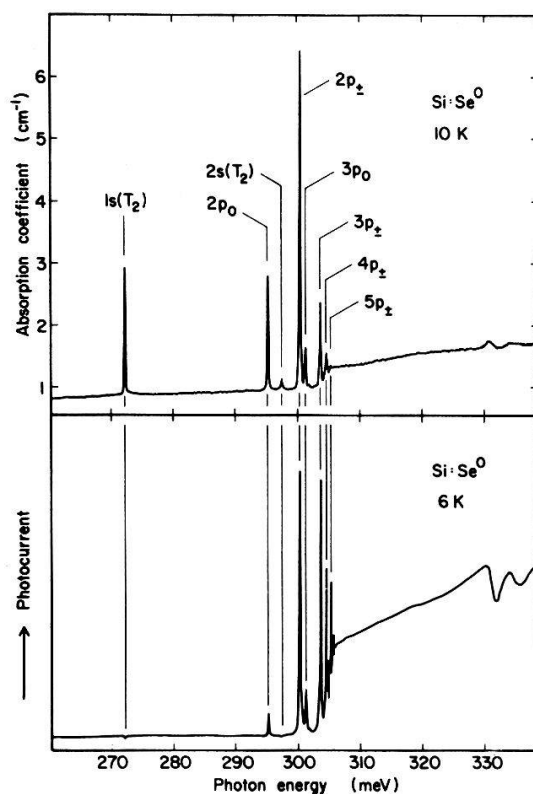


Fig. 3: Fourier absorption and photoconductivity spectrum of selenium doped silicon¹⁶⁾.

Since the binding energies of states originating from the Rydberg series are well known from EMT, the assignment of the line spectrum is straightforward. It is readily seen from the absorption spectrum that both the odd-parity and the EMT-forbidden, but symmetry-allowed, transitions really occur in the absorption spectrum. It should, however, be noted that, for example, the $1s(T_2)$ and $2s(T_2)$ lines are missing in the photoconductivity spectrum probably due to lifetime effects. From a line spectrum such as the one shown in figure 3, the binding energy of the ground state is easily obtained, e.g. by measuring the excitation energy for the transition $1s(A_1) \rightarrow 2p_{\pm}$ and adding the EMT binding energy of the $2p_{\pm}$ state²⁾ which is 6.40 meV. Once the ioniza-

tion limit is known, the binding energies of all excited states are readily derived.

From the energy spacing of the excited states, we know that the center is neutral when occupied. By counterdoping the sample with shallow acceptor levels, an ionized version of the center can be seen in absorption. Evidence that these two energy levels originate from the neutral and ionized version of a double donor is obtained from junction space charge techniques¹⁷⁾. Neither absorption measurements nor junction techniques, however, give information on the nature of the center, i.e. whether the center is selenium related or not. This information had therefore to be obtained from ESR measurements. The ESR spectrum was then correlated with the energy position of the center by illuminating the sample with monochromatic light of different photon energies. Owing to the different time dependence of the photon-induced valency change of the ESR active center for different photon energies, the spectral distribution of the photoionization cross section could be measured¹⁰⁾. Since these results agree with those spectra obtained from junction measurements, we conclude that the ESR signal originates from a selenium related double donor in a tetrahedral surrounding.

The energy level giving rise to the line spectrum of figure 3 has a ground state binding energy of 306.6 meV^{8,11)}. The corresponding value for the ionized version is 593.2 meV¹¹⁾. Similar measurements were performed on sulfur and tellurium doped samples^{10,16,18)}. The binding energies of ground states and several excited states obtained for sulfur, selenium and tellurium related double donors on tetrahedral sites are summarized in Table 1:

Binding energies (meV) for chalcogenides in silicon

| | S ⁰ | S ⁺ | Se ⁰ | Se ⁺ | Te ⁰ | Te ⁺ |
|---------------------|----------------|----------------|-----------------|-----------------|-----------------|-----------------|
| 1s(A ₁) | 318 | 614 | 307 | 593 | 199 | 411 |
| 1s(T ₂) | 35 | 184 | 35 | 164 | 39 | 177 |
| 2p ₀ | 11 | 45 | 12 | 45 | 12 | 46 |
| 2p _± | 6 | 26 | 6 | 26 | 6 | 26 |

Although different dopings result in centers with different ground state binding energies, it is readily seen that the energies of the Rydberg series are very similar and in agreement with EMT for all three chalcogenides. Figure 4 shows that this is not only valid for lower excited states, but also for higher excited states.

Chalcogenides form different centers in silicon¹⁹⁾. Apart from isolated double donors, several other chalcogen-related centers, such as pairs and other more complicated complexes, are observed in relatively high concentrations. If the defect

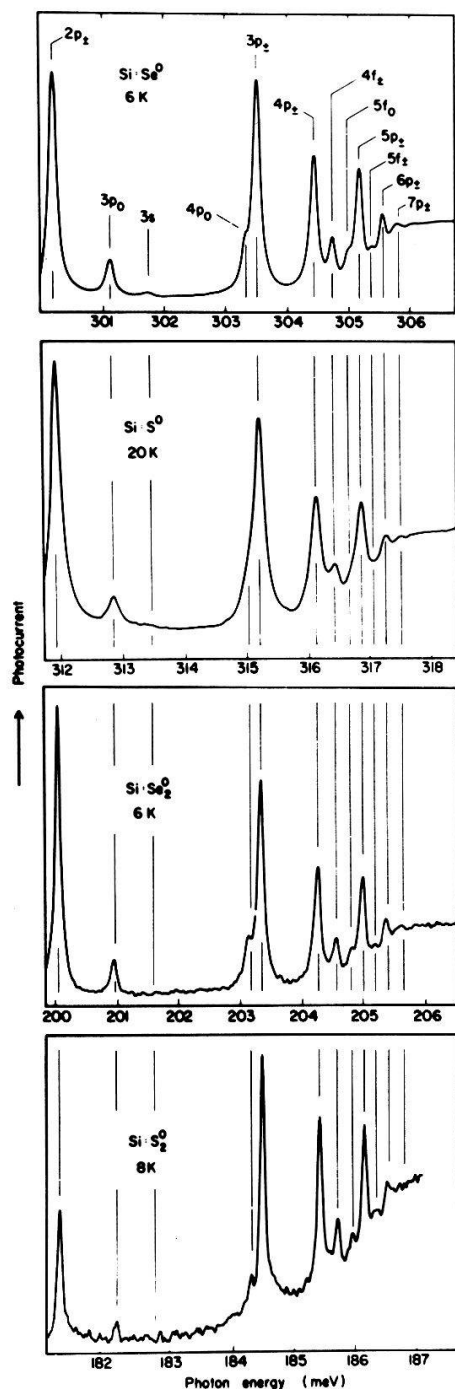


Fig. 4: Photoconductivity spectra of sulfur and selenium doped silicon¹⁶⁾, showing transitions from the ground state to the excited states of isolated, neutral impurities on tetrahedral sites (Si:S^0 , Si:Se^0) and of impurity pairs on trigonal sites (Si:S_2^0 , Si:Se_2^0).

consists of a pair instead of an isolated substitutional chalcogen atom, the local symmetry is lowered from tetrahedral to trigonal. An electron far away from the pair-defect only feels the isotropic Coulomb potential. Excited states such as p states are therefore essentially unaffected as can be seen by the data presented in figure 4. Although p states are not changed by the lowering of the symmetry, quite radical effects are observed for multivalley split s states.

A closer inspection of figure 4 reveals that Fourier spectroscopy is indeed a high resolution measurement technique. An enlargement of the selenium data (figure 5) shows that excited states up to $7p_+$ can be studied, and details, such as $3s(T_2)^+$ and $5f_0$ states, are clearly observed.

When photoexcitation can result either in a final discrete state or in a continuum state of the same energy, any small interaction between such states will result in a marked resonance structure in the photoexcitation spectrum, commonly known as a Fano resonance¹⁵⁾. The two interacting processes, which have been observed in sulfur, selenium and tellurium doped silicon, are a no-phonon excitation from the ground state to the continuum and a transition from the ground state to a bound excited state accompanied by emission of a phonon (figure 6)^{16,20)}. The structure studied is therefore observed above the ionization limit (C.B.).

It has earlier been shown that in silicon, in zeroth order approximation, only intervalley phonons are allowed in intraband

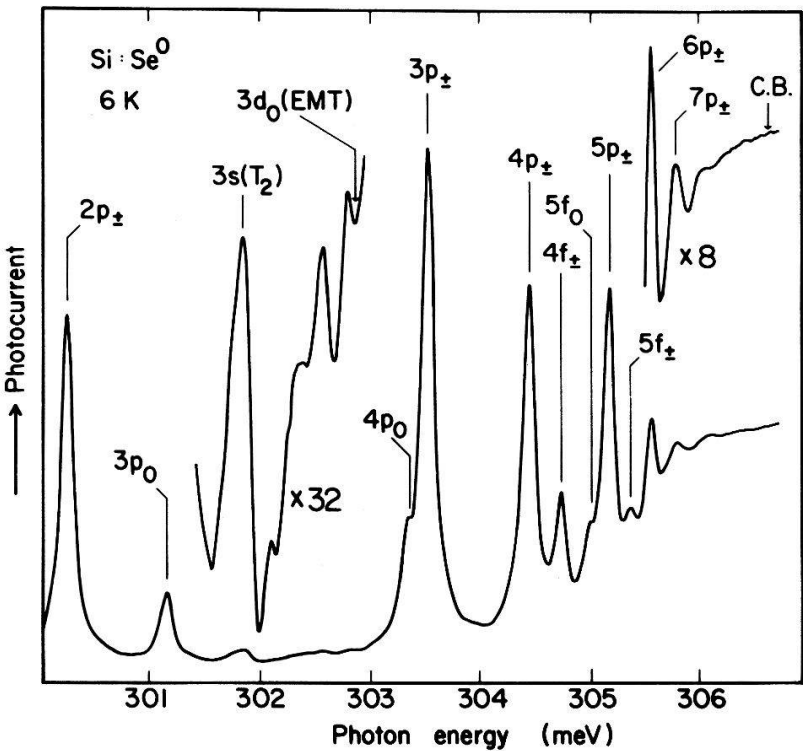


Fig. 5: Enlargement of part of the Si:Se⁰ photoconductivity spectrum of figure 4.

electron-phonon interaction 21) (figure 7), and that the g LO(Δ_2') phonon of 63.3 meV and the f TO(S_1) phonon of 59.0 meV should couple with comparable strength to electrons, whereas the f LA(S_1) phonon of 46.1 meV should interact much less than the other two phonons. Figure 8 shows that this is indeed observed for all three chalcogenides. The arrows A, B and C mark the excitation energies from the ground state 1s(A₁) to the 1s(T₂) state plus the energies of the three phonons mentioned above.

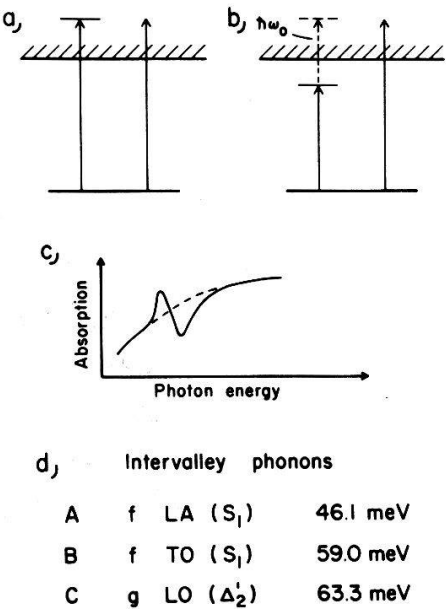


Fig. 6: (a) No-phonon and (b) phonon assisted transition in chalcogenide doped silicon. (c) Fano resonances. (d) Intervalley phonons.

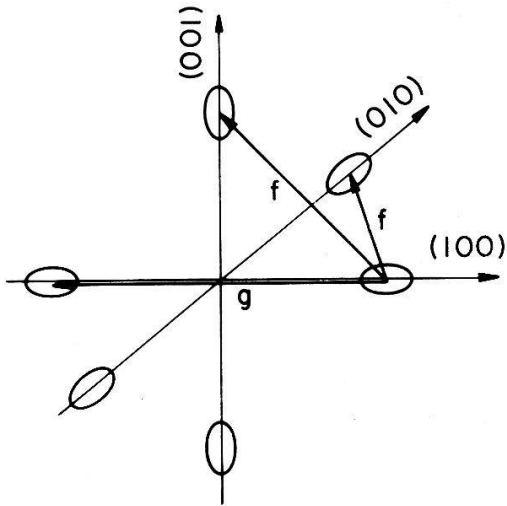


Fig. 7: A schematic view of the constant energy surfaces of the six conduction band minima in silicon, showing the two possible types of intervalley scattering.

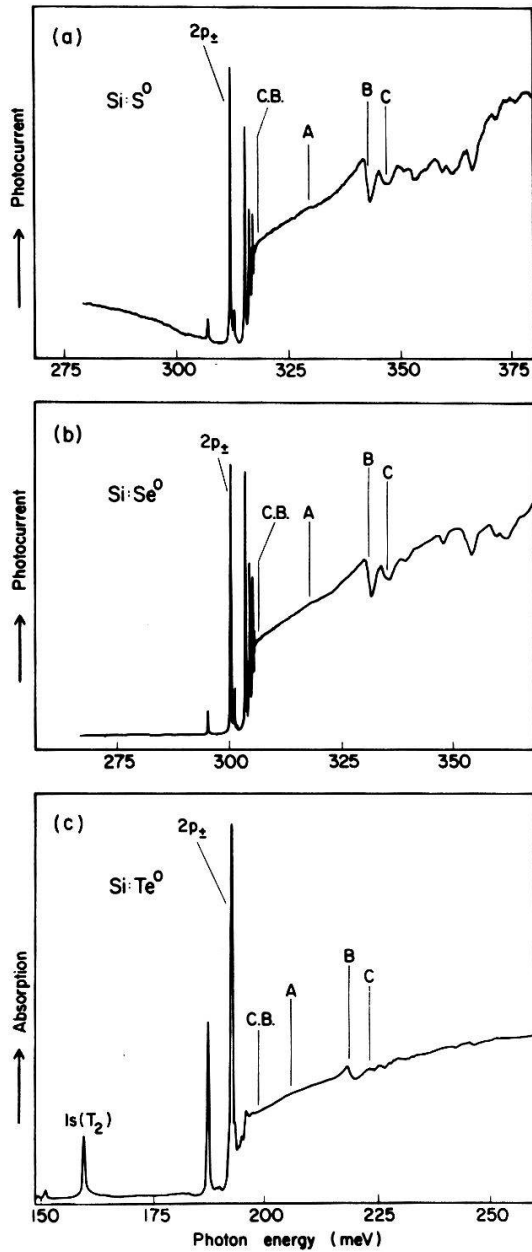


Fig. 8: Fourier absorption and photoconductivity spectra of Si:S^0 , Si:Se^0 and Si:Te^0 . C.B. marks the ionization limit. The arrows A, B and C mark the excitation energies from the ground state $1s(A_1)$ to the $1s(T_2)$ state plus the energies of the three intervalley phonons ¹⁶⁾.

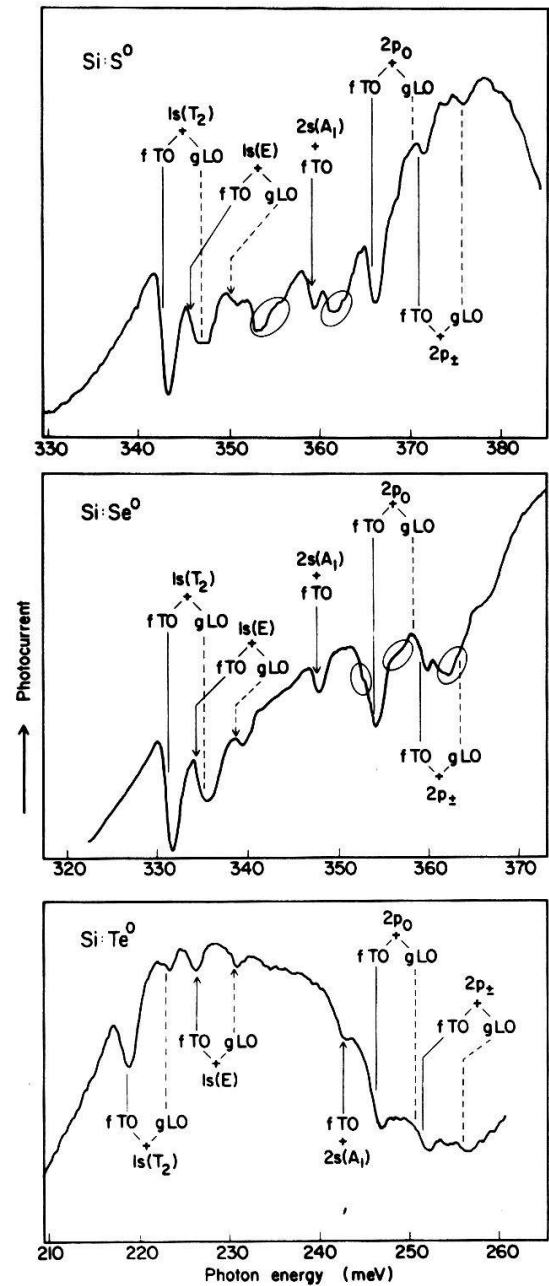


Fig. 9: Partial enlargements of the spectra presented in figure 8, showing the Fano resonances ¹⁶⁾.

The weaker coupling of the $f LA(S_1)$ phonon is quite evident.

A closer inspection of the spectral distributions above the ionization limit reveals highly structured spectra, which contain information not only on states such as $1s(T_2)$ and p states, which can be excited from the ground state by EMT and symmetry allowed transitions, but also on states such as $1s(E)$ and $2s(A_1)$ states (figure 9), which cannot be excited by no-phonon transitions²⁰⁾. Again, the assignment of the resonances is fairly straightforward, since the allowed transitions are known from direct optical absorption measurements. A detailed evaluation of such spectra gives accurate values for the binding energy of excited states, including those which are unobserved in no-phonon absorption. The binding energy (in meV) of low-lying D^0 states in sulfur, selenium and tellurium doped silicon^{16,20)} are summarized in Table II:

Binding energies (meV) of low-lying D^0 states in chalcogenides doped silicon

| | $1s(A_1)$ | $1s(T_2)$ | $1s(E)$ | $2s(A_1)$ |
|--------|-----------|-----------|---------|-----------|
| S^0 | 318.3 | 34.6 | 31.6 | 18.4 |
| Se^0 | 306.6 | 34.4 | 31.2 | 18.0 |
| Te^0 | 198.8 | 39.1 | 31.6 | 15.2 |

In order to demonstrate the advantage of FPAS compared with Fourier absorption and Fourier photoconductivity spectroscopy, the enlarged Te^0 spectrum obtained with these three different measurement techniques is shown in figure 10 for comparison¹⁶⁾. The higher signal to noise ratio of the FPAS is quite obvious in spite of the higher measuring temperature.

Fano resonances have been observed not only for isolated centers, but also for complexes²⁰⁾. As an example, figure 11 shows FPAS spectra above the ionization level for neutral sulfur and selenium pairs¹⁶⁾. Since the symmetry is lowered and, hence, the energies of the multivalley split s states are different for pairs, the structures observed are quite different compared with those for isolated centers. Nevertheless, it is interesting to note that the same phonons are involved.

In studying double donors, samples have been prepared where the Fermi level lies between the ground state of the neutral and ionized versions. In such samples the multivalley split s bands, the Rydberg series and the Fano resonances of both versions can be observed simultaneously¹⁶⁾ (figure 12).

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