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SULFUR-HYDROGEN DONOR COMPLEXES IN SILICON

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ABSTRACT

We demonstrate for the first time that hydrogen and sulfur combine in silicon to form complexes with donor levels in the gap. Well-characterized sulfur-doped silicon is heated at 1280° C in hydrogen gas and then quenched. Fourier-transform infrared-absorption spectroscopy from 500 to 3000 cm^{-1} at 0.5 cm^{-1} resolution and 1.7 K sample temperature reveals a decrease in sulfur-related donor concentrations and the appearance of several novel features. First, the ordinarily-weak $S_c(X_2)$ spectrum is greatly enhanced. Deuterium substitution shifts line-center frequencies by 2.2 cm^{-1}, showing that hydrogen is incorporated in this defect and does not merely catalyze its formation. Second, two closely-spaced donor levels are created. Deuterium substitution increases their 3 cm^{-1} separation by 0.5 cm^{-1}, demonstrating the presence of hydrogen in these centers, too. The relative concentration of the deeper level increases with quenching rate. Finally, two isotope-independent donor levels appear within 3 cm^{-1} of $S_c(X_3)$'s level.

I. INTRODUCTION

When hydrogen passivates the electrical activity of single donors and single acceptors in silicon, their electronic spectra are lost, so experimental information on microscopic structure comes solely from the study of local vibrational modes[1] and channeling[2,3]. On the other hand, electrical activity remains when partial passivation occurs for impurities which bind more than one carrier at low temperature. The electronic spectra of the partially-passivated double-acceptor[4,5] Be in Si and the triple-acceptor[6] Cu in Ge have shown that these exotic complexes tunnel or rotate among equivalent configurations. Similar studies on like systems in Ge have led to competing motional[7,8,9] and static interpretations[10,11]. Because hydrogen-related systems which retain electrical activity have proven to be so intriguing and controversial, there is value in searching for other examples. This is especially true for combinations of hydrogen and double donors, since systems of this type have not been as extensively studied.

The best understood double donors in silicon are the chalcogen impurities, sulfur, selenium and tellurium[12,13], and these impurities form a variety complexes. For sulfur, infrared (IR) spectra reveal absorption-line series for the isolated donor, the pair, and five sulfur-related complexes labeled $S_c(X_n)$ where n=1,2,3,4,5. The relative concentration of the various centers depends on the thermal history of the samples, but ordinarily the concentrations of $S_c(X_2)$ and $S_c(X_4)$ are very low and their absorption lines extremely weak[13,14].

Hydrogen passivation of S_2^0 and S_2^+ in silicon has been observed via Deep Level Transient Spectroscopy (DLTS) by Pensl et al.[15,16], but they found no new levels. This does not rule out the possibility of partial passivation, however, since the levels so created may be insufficiently deep for DLTS to detect. A more effective way to search for such shallow levels is by IR-absorption spectroscopy, the technique employed here.

Our result is the first identification of sulfur-hydrogen related donors in silicon. Strong absorption spectra show that five levels are created when hydrogen is diffused into sulfur-doped silicon, and all are shallower than either S_2^0 or S_2^+. One set of lines exactly coincides with the spectrum of $S_c(X_2)$, strongly suggesting that the $S_c(X_2)$ structure includes hydrogen, and a well-resolved isotope effect confirms this. Two of the donors were the subject of a previous study by us[17], but we demonstrate here for the first time the isotope effect that substantiates identification as (S,H) centers. The last two donor spectra are energetically near that of $S_c(X_3)$ and appear to be isotope independent.

II. EXPERIMENTAL DETAILS

Polished 1600-2000 Ω-cm float-zone Si slabs are sealed in quartz ampoules together with 8 mg of sulfur and 300 torr of He, heated 40-50 hours at 1280 °C, and quenched by pulling the ampoules out into the air or by merely turning off the furnace. Spectra are collected from 500 to 3000 cm^{-1} at 0.5 cm^{-1} resolution using a Brüker Fourier-transform IR interferometer while the samples are cooled to 1.7 K in a Janis varitemp optical-access cryostat with ZnSe and NaCl windows. Then the samples are resealed in

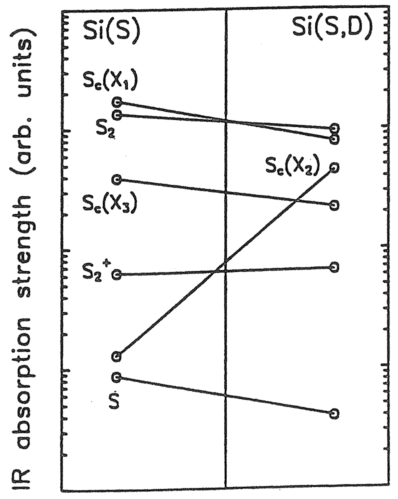

Figure 1. Sulfur-related donor concentrations before and after deuteration.

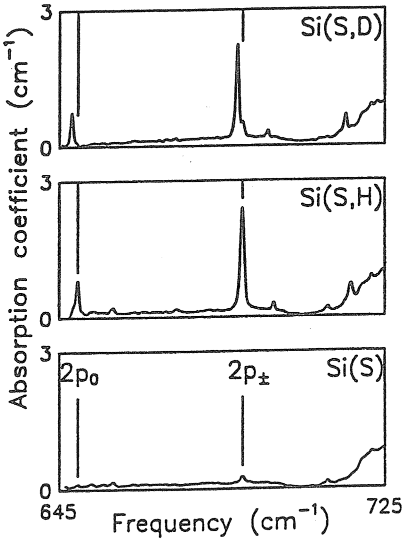

Figure 2. Absorption spectra of Si(S), Si(S,H) and Si(S,D). The frequency positions of $S_c(X_2)$'s two strongest lines are indicated.

quartz ampoules together with 700 torr of H_2 or D_2 gas, heated 15-30 minutes at 1300 °C, and quenched as before or in liquid nitrogen. Finally, spectra are taken again.

III. RESULTS

A. $S_c(X_2)$ OR (S,H)[92meV]

Figure 1 shows the effect of deuteration on sulfur-related donor concentrations. The integrated area of each species' $2p_0$ line (or half its $2p_\pm$ line) is taken as a measure of concentration and is plotted on a log scale over four decades. Solid lines connect values before deuteration (left side) with values after deuteration (right side), and each donor species is labeled. The neutral donors S, $S_c(X_1)$ and $S_c(X_3)$ decrease in number by a factor of about 2, and S_2 becomes about 1.4 times more scarce. Only S_2^+ seems relatively unperturbed. A simple Fermi-level effect can not explain figure 1, since the various donor levels are widely dispersed in the gap[14], so decreases in absorption strength must really imply concentration decreases.

In addition, figure 1 shows a surprising 34-fold increase in the concentration of $S_c(X_2)$. Hydrogen must play a special role in $S_c(X_2)$, either as catalyst or physical constituent. We investigate these possibilities next.

Absorption spectra from 645 to 725 cm^{-1} for Si(S), Si(S,H) and Si(S,D) samples are plotted in the bottom, middle and top portions of figure 2, respectively. Pointers indicate the known[14] frequency positions of $S_c(X_2)$'s $2p_0$ and $2p_\pm$ lines. For Si(S) two small peaks coincident with the pointers reveal a weak concentration of $S_c(X_2)$.

The middle spectrum in figure 2 demonstrates the effect of hydrogenation for a sample with similar initial concentrations of S-related centers as the sample used for figure 1. Here the $S_c(X_2)$ spectrum is strong, though it was too weak to be observed prior to hydrogenation. Again, our conclusion is that

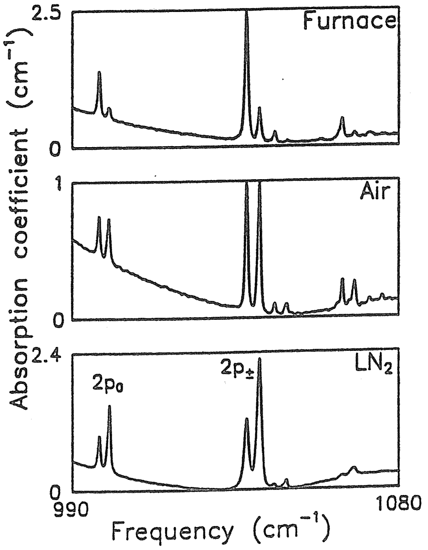

Figure 3. (S,H)[135.07meV]and (S,H)[135.45meV] donor absorption spectra and quench dependence. Labels give the method of quench.

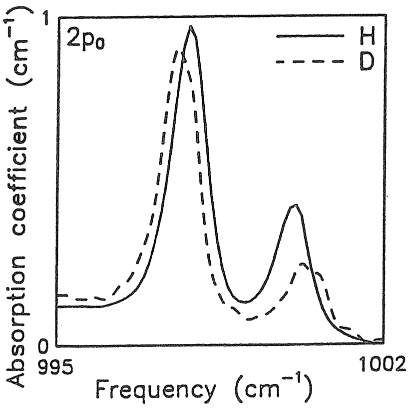

Figure 4. Isotope effect for (S,H)[135.07meV]and (S,H)[135.45meV] donor $2p_0$ lines.

hydrogen either catalyzes $S_c(X_2)$ formation, or $S_c(X_2)$ contains hydrogen.

The top spectrum in figure 2 shows the effect of isotope substitution. Here the strong lines are red-shifted with respect to the $S_c(X_2)$ markers by 2.2 cm^{-1}. Weak shoulders do line up with the markers, but these features existed before deuteration (bottom spectrum). The isotope shift (0.3%) is large[18] for the electronic spectrum of a donor, so $S_c(X_2)$'s ground state must strongly couple to one of hydrogen's nuclear degrees of freedom. This requires that hydrogen be within the well-localized ground orbital, so that hydrogen must be regarded as a physical constituent of $S_c(X_2)$.

This result mandates a more descriptive label than "$S_c(X_2)$". We propose the name $(S,H)_c$[92 meV], instead, where the bracketed quantity is the binding energy[14]. This nomenclature is based on definite physical characteristics and clearly distinguishes the various (S,H) complexes discussed in this paper.

B. $(S,H)_c$[135.07 meV] AND $(S,H)_c$[135.45 meV]

Figure 3 presents spectra from 990 to 1080 cm^{-1} for three deuterated sulfur-doped samples. Each spectrum shows two donor absorption-line series separated from each other by about 3 cm^{-1}. Ground-state binding energies of 135.07 and 135.45 meV are found by adding the theoretical $2p_\pm$ level binding energy (6.40 meV) to the measured 1s to $2p_\pm$ transition frequency (the strongest line in each series).

Each of the samples used for figure 3 was quenched at a different rate. The label "furnace" signifies a slow quench within a cooling furnace. Increasingly rapid quenches are labeled "air" and "LN_2". It is clear that the relative concentration of the two donors depends on the quenching rate and that a rapid quench favors the donor with the deeper level. One possible explanation is that the two levels arise from different structural configurations of the same complex.

Figure 4 shows the isotope effect. The absorption coefficient of the $2p_0$ lines is plotted versus frequency for Si(S,H) (solid line) and Si(S,D) (dashed line). Apparently, deuterium substitution causes the level separation for 135.07 meV and 135.45 meV donors to increase by about 0.5 cm^{-1}. Yet this effect is the same size as the experimental resolution and only 0.04% of the binding energy, so closer inspection is required.

The center-frequency separation of each transition for the 135.07 meV and 135.45 meV donors in all samples is given in figure 5. Data for hydrogenated (deuterated) samples are represented by squares (circles), and solid lines connect average values. Transitions are labeled and arranged on a scale proportional to the theoretical final-state binding energy[14]. Frequency separations are consistently larger in deuterated samples, so the isotope effect is evidently real. Hence, we conclude that hydrogen is a constituent of $(S,H)_c$[135.07 meV] and $(S,H)_c$[135.45 meV].

Figure 5 also reveals the curious fact that the peak separation is smaller for p_0 lines than for $p_\pm$ lines. Generally, the binding energies of shallow excited states do not vary from donor to donor[14,19], but here is a contrary example. One possible explanation is a difference for the two donors in the longitudinal and/or transverse effective mass, since it is these masses which determine the relative binding energies of $2p_0$ and $2p_\pm$ levels.

C. (S,H)[82.4meV] AND (S,H)[82.6meV]

Figure 6 presents spectra from 565 to 650 cm^{-1} of Si(S) and Si(S,D) samples. The line spectrum of only $S_c(X_3)$ is present for Si(S), but for Si(S,D) two additional donor spectra appear. The binding energies of the two new centers are 82.4 and 82.6 meV. Their concentration relative to $S_c(X_3)$ and to each other is found to depend on the quench rate. In addition, figure 6 shows two lines on the high-frequency side of $2p_0$ which do not belong to any donor discussed so far. Hydrogenated samples give similar spectra, but there is no resolved isotope effect. Perhaps the new donors are merely perturbed versions of $S_c(X_3)$.

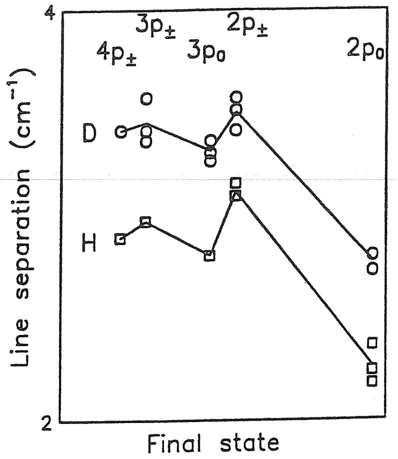

Figure 5 Isotope effect for (S,H)[135.07meV] and(S,H)[135.45meV] donors. The separation between peaks of each donor is plotted for each transition. All available data is plotted.

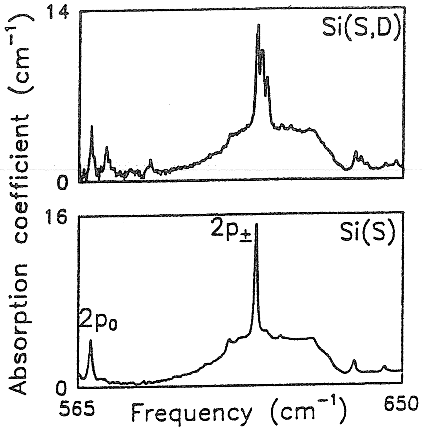

Figure 6. Absorption spectra of Si(S) and S(S,D). The sharp lines in Si(S)'s spectrum belong to $S_c(X_3)$. The additional lines in S(S,D)'s spectrum belong to the donors (S,H)[82.4meV] and (S,H)[82.6meV].

IV. DISCUSSION AND SUMMARY

We have demonstrated that five donor levels appear when hydrogen is diffused into sulfur-doped silicon. Three of the levels, including one that is identical to $S_c(X_2)$, display isotope effects that confirm the presence of hydrogen in their structure. The (S,H) donors may be partially-passivated versions of one or more of the donors S, S_2, $S_c(X_1)$ and $S_c(X_3)$, whose concentrations decrease after hydrogenation. The temperature dependence of the (S,H) centers has also been measured but is not presented here since it reveals no additional levels besides the donor ground states. In other words, there is no evidence that the (S,H) donors have the kind of dynamic motion that enriches the spectra[4,5] of Si(Be,H) and[6] Ge(Cu,H_2).

In conclusion, (S,H) centers appear to be of fundamental interest. IR uniaxial stress measurements may reveal configurational degeneracies and site symmetries. If the (S,H) donors are paramagnetic, which would be the case for partially-passivated double donors, sharp spin resonances may be expected. This is not expected to be true for partially-passivated acceptors[20]. In addition, comparision of IR absorption strength with published[15,21] spectra of Si:Se^0, for which the concentration is roughly known, shows that (S,H) donor concentrations may be as high as 10^{15}-10^{16} cm^{-3}. Thus, one feature of our study is that a set of hydrogen-related donors have been found which still retain electronic spectra and which are in sufficiently high concentration so that formidable spectroscopic techniques, such as IR absorption and electron-spin resonance, may be employed to unravel structure and gain a better understanding of these and similar defects.

V. ACKNOWLEDGMENTS

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