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Infrared spectral hole burning of sulfur-hydrogen deep donors in a Si:Ge crystal

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Spectral holes which persist for ~5 msec have been produced in the spectrum of a sulfur-hydrogen complex in a Si–0.1 at.% Ge alloy crystal maintained at 1.7 K. Measurements which combine an infrared laser pump with a Fourier-transform spectrometer probe show that the hole burning is due to migration of electrons from the S-H centers to shallow traps. The large observed hole width (4.6 cm^{-1}) is attributed to spectral diffusion by resonant excitation transfer. The lack of temperature dependence of the hole burning of the $2p\pm$ line below 30 K suggests that excitation transfer is also responsible for the ionization of laser-excited centers in the hole-burning process.

Persistent spectral hole-burning (PHB) effects,[1,2] which are ascribed to photochemical (electron migration) and nonphotochemical (defect reorientation or host rearrangement) mechanisms[3] (NPHB) have been identified in the electronic spectra of polymers, glasses, and crystals and in the vibrational spectra of molecular defects in ionic crystals. The observation of persistent spectral hole burning of color centers in diamond[4] raises the possibility that persistent effects may be a common occurrence for impurity states in semiconductors. A likely source of PHB in semiconductors is the electron-migration mechanism which should be applicable to the inhomogeneously broadened electronic spectra of any kind of defect in semiconductors. On the other hand, NPHB due to defect reorientation can be expected only for the defects which have configurational degeneracy.[5] We report here the first observation of persistent hole burning in a silicon-based crystal.

In the first experimental search for persistent hole burning in an elemental semiconductor we have examined a deep donor complex (S-H) in Si and in a Si:Ge crystal which has electronic transitions coincident with CO_2 laser lines. In principle, both PHB and NPHB can occur for this low-symmetry center. Persistent hole burning has been observed for both the $2p\pm$ and $2p_0$ transitions of the deep-level center in the Si:Ge alloy but not in the pure Si host. The spectroscopic results are consistent with the electron-migration model and the different response for the pure and alloy host is caused by the availability of low-lying traps.

Sulfur double donors have been introduced into pure float-zone-refined silicon wafers using standard diffusion-doping techniques. The subsequent formation of S-H defect complexes by annealing in H_2 gas has been used to produce new sets of electronic spectra in the infrared region. One of these S-H defect centers is found to have near-perfect coincidence with the available $^{12}CO_2$ or $^{13}CO_2$ laser lines. Finally, this same S-H center has been prepared in a Czochralski-grown Si–0.1 at.% Ge alloy so that the defect spectrum in the extreme inhomogeneous limit could be studied.

Persistent spectral effects have been probed with two different experimental arrangements. They are as follows: (1) using a tunable semiconductor diode laser (SDL) to probe spectral changes caused by the illumination of a CO_2 pump laser; or (2) probing with a Fourier-transform spectrometer (FTIR) for broadband spectral changes caused by the illumination of a CO_2 pump laser. Because the S-H holes have turned out to be broad, this last technique has provided the most complete information on the system dynamics. Scheme (1), however, is useful near the pump frequency, where scattered laser light interferes with the performance of the FTIR.

The sample is immersed in superfluid helium at 1.7 K in an optical-access cryostat. Appropriate cold bandpass interference filters are used to cut off the unfavorable thermal radiation in the ionization spectral region since in the 10-μm region this radiation will erase in a very short time any memory effect.

Hole burning has been observed for both S-D and S-H centers in the Si:Ge alloy crystal where a CO_2 laser (typically ~100 mW/cm^2) can be used in conjunction with a tunable SDL or FTIR spectrometer. The effect is not caused by transient saturation since this mechanism is observed to become important at the much higher pump intensity of ~100 kW/cm^2 for the $1s(A_1) \rightarrow 2p\pm$ transition.

Figure 1 shows the spectra of the S-D complex in pure Si and Si:Ge alloy crystal, as well as the associated laser-induced spectral changes. Hole-burning experiments on the $2p\pm$ line have been performed using pump frequencies ranging over the entire inhomogeneous line and beyond. Most of the $^{12}CO_2$ laser lines in the $9P$ branch have been employed. Figures 1(c) and 1(e) show the resulting spectral changes for some representative pump frequencies. The hole-burning effect appears to be independent of pump intensity for intensities between roughly 20 mW/cm^2 and 1 W/cm^2. For intensities below about 20

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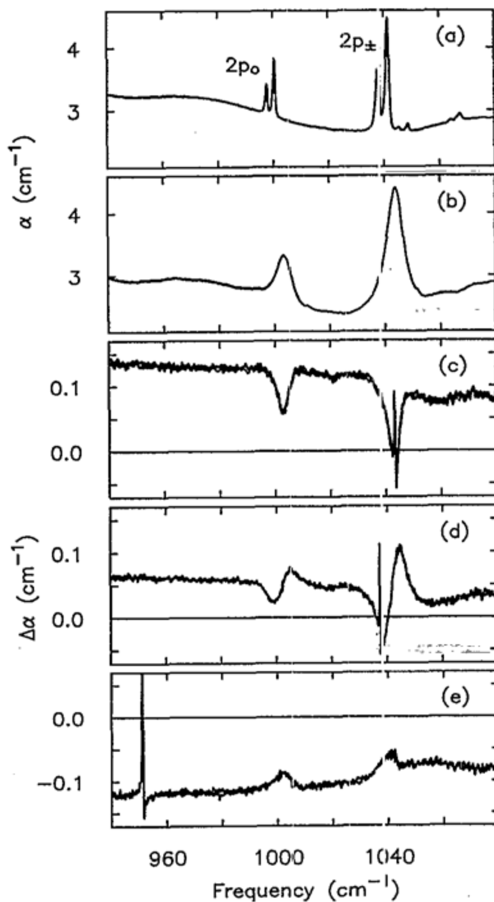

FIG. 1. Absorption spectra of the S-D centers in (a) pure Si and (b) Si:Ge alloy crystal. In (a) the two absorption series separated by $\sim 3\ cm^{-1}$ are attributed to different configurations of S-D center; rapid quenching after the deuterium diffusion favors the center with the higher frequency absorption series. In the mixed crystal, the absorption shifts slightly to higher frequency and the two series merge into broad inhomogeneous lines, FWHM $=7.1\ cm^{-1}$. Samples were prepared in a similar manner: S diffusion at 1280 °C for $\sim$50 h followed by D diffusion at 1280 °C for 30 min. Similar results were obtained using hydrogen instead of deuterium. (c)–(e) FTIR spectra showing laser-induced spectral changes in the S-D absorption. Plotted is the change in absorption coefficient produced by pumping with the following CO_2 laser lines: (c) 9P(24), 1043.16 cm^{-1}; (d) 9P(30), 1037.43 cm^{-1}; and (e) 10P(12), 951.12 cm^{-1}. The sharp upward spikes in the spectra are due to scattered laser light and serve in effect as markers of the pump frequency.

mW/cm^2, the hole depth decreases.

When the pump frequency is near the center frequency of the inhomogeneous $2p\pm$ absorption line, as in Fig. 1(c), holes with full width at half maximum (FWHM) equal to 4.6 cm^{-1} appear in both the $2p\pm$ and the $2p_0$ lines. For both holes, the hole depth corresponds to an absorption change of about 10% of the total absorption strength of the line. Figure 1(d) shows typical results for off-center pumping. The center frequency of the $2p\pm$ hole is not exactly at the pump frequency, but shifted by as much as 0.5 cm^{-1} toward the center of the inhomogeneous line. Another hole appears in the corresponding place on the inhomogeneous profile of the $2p_0$ line. In addition to the holes, antiholes (absorption increases) spread over the two inhomogeneous lines are also produced. Hole growth and decay rates have been determined by chopping the CO_2 pump beam while monitoring the time-dependent transmitted intensity of the continuous wave (cw) SDL probe beam tuned to the center frequency of the hole. Hole growth and decay times are both on the order of 5 ms at 1.7 K with pump intensity of 0.5 W/cm^2.

The hole width and depth quoted above is for the case in which pump and probe beams are polarized parallel to each other along the same [100] crystal axis. When the pump and probe beam are polarized perpendicular to each other, the observed hole width is 5.5 cm^{-1}. This increased hole width for the perpendicularly polarized case is attributed to impurity-induced random splitting of the excited-state degeneracy. This splitting should not affect the hole width in the parallel polarization configuration since in this case the probe monitors transitions to the same p-states that were involved in the hole burning.

Hole-burning experiments have also been performed on the $2p_0$ line using the $^{13}CO_2$ 9P(16) laser line at 1004.28 cm^{-1}. As can be seen in Fig. 2, at 1.7 K no holes are observed. A shallow hole first becomes apparent at 15 K and reaches maximum depth by 25 K. This temperature-dependent behavior contrasts sharply with that observed for holes produced by pumping the $2p\pm$ line; $2p\pm$ holes show no measurable temperature dependence between 1.7 and 30 K. Above 30 K, both kinds of holes broaden and weaken with increasing temperature, as do the absorption features themselves.

In addition to the well-defined holes and antiholes directly associated with the $2p$ absorption lines, laser pumping also induces broad-band spectral changes extending over hundreds of cm^{-1}. When the pump frequency is within the inhomogeneous profile of the $2p\pm$ line, a broadband absorption increase results. [Note base-line positions in Figs. 1(c) and 1(d).] A broadband absorption decrease is produced for pump frequencies well below the $2p\pm$ line [Fig. 1(e)]. These broadband changes have been observed with both the FTIR and SDL probe techniques.

The electron-migration mechanism provides a natural explanation for the observed spectral changes. In this model, S-H centers of a particular ground-state energy, determined by the pump-laser frequency, are selectively excited. From the excited state electrons can reach the conduction band, where they migrate freely until they are trapped, either by another unoccupied S-H center, or by some other kind of impurity center. The rate at which electrons are excited from the traps back into the conduction band and the rate at which they decay back into the S-H centers determines the persistence time of the spectral holes.

The appearance of antiholes can also be understood in terms of the migration model. The samples used in these experiments are partially compensated, so that there are many empty as well as occupied donor centers. If the electrons from the hole-burned S-H centers are captured

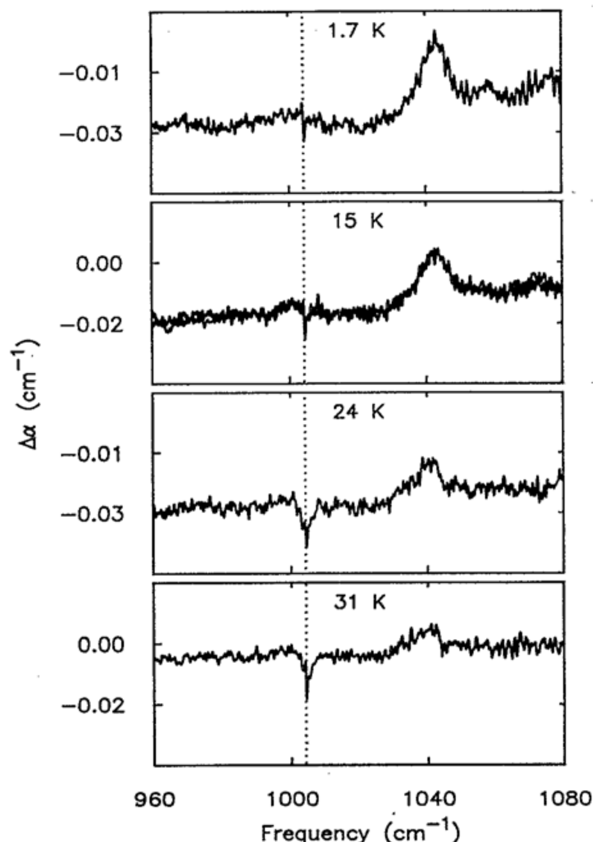

FIG. 2. Temperature dependence of the spectral hole produced by pumping the $1s(A_1)\rightarrow 2p_0$ transition. The pump frequency, 1004.28 cm^{-1}, near the center of the inhomogeneous $2p_0$ line, is indicated by the dotted vertical line. Sharp spikes at the pump frequency are due to scattered light. The feature centered at $\sim$1045 cm^{-1} is the $2p\pm$ antihole, due to the filling of compensated S-H centers with electrons liberated by ionization of shallow donors. A similar feature associated with the $2p_0$ line is visible in the 1.7 and 15-K plots.

by other, already empty S-H centers, an increase in absorption, i.e., an antihole, over the entire inhomogeneous profile of each of the S-H lines should result. Such broad antiholes can be seen in Fig. 1(d).

If, on the other hand, electrons from the hole-burned centers are trapped by unoccupied shallow donor centers, the absorption strength associated with those shallow centers will increase. In particular, the broadband absorption associated with the ionization of those centers will increase, even though the laser radiation which produces the hole burning can also ionize the shallow donors, because direct photoionization of the shallow donors is much less efficient than the strongly allowed $1s(A_1)\rightarrow 2p\pm$ pumping involved in the hole-burning process. Figures 1(c) and 1(d) show that by hole burning the S-H centers, the pump radiation makes available more electrons for the unoccupied shallow donors to trap than it removes from occupied shallow donors, the net effect being that the occupation of the shallow donors increases when the pump laser is on.

If, as in Fig. 1(e), the pump-laser frequency is not coincident with any absorption lines of the S-H centers, ionization of the shallow donors can still take place, but no hole burning occurs to make electrons available to refill the shallow centers. The net result in this case is that the broadband ionization absorption associated with the shallow centers is decreased [Fig. 1(e)]. The small antiholes on the S-H $2p\pm$ and $2p_0$ lines which appear in Fig. 1(e) are attributed to filling of empty S-H centers with electrons liberated by the photoionization of shallow donors.

The mechanism by which the electrons reach the conduction band from the S-H excited states is not clear at present. Any model must be able to explain both the strong temperature dependence of the $2p_0$ hole burning and the temperature independence of the $2p\pm$ hole burning below 30 K. The $2p\pm$ and $2p_0$ states are 6.4 meV ($\sim$74 K) and 11.5 meV ($\sim$133 K) below the conduction band,[6] respectively, and so direct thermal ionization to the conduction band at 1.7 K is unlikely from either state. Moreover, this mechanism predicts activation energies from the two states which differ only by a factor of 1.8, as opposed to the factor of at least 10 implied by the observed temperature dependence.

Resonant energy transfer provides another, perhaps more promising, mechanism by which electrons can reach the conduction band. The transfer of energy between centers permits an upward transition when neighboring centers are both in an excited state since the de-excitation of one center to the ground state is accompanied by the excitation of the second to the conduction band to conserve energy. The temperature independence of the $2p\pm$ hole burning at low temperatures supports this mechanism. If the resonant transfer rate is much larger than the multiphonon decay rate, a large excited-state population (and hence high pump intensity) would not be necessary for this mechanism to work; multiple transfers would allow two excitations to wander in the crystal until they encountered one another.

In the resonant-transfer model, two factors can account for the different hole-burning behavior of the $2p_0$ and $2p\pm$ states. First, the resonant transfer rate varies as the square of the effective concentration of the centers, so the $2p\pm$ resonant transfer would be four times as effective as the $2p_0$ transfer because of the degeneracy factor. Second, there is reason to believe that for this center the multiphonon decay rate of the $2p_0$ state may be much greater than for the $2p\pm$ state; the $1s(A_1)\rightarrow 2p_0$ transition (1004 cm^{-1}) of the S-H center is almost exactly twice the energy of the LO phonon in Si (maximum density of states is at 504 cm^{-1}).[7] Thus the $2p_0$ state may decay rapidly by emission of two LO phonons before resonant transfer to another site can occur. Marked lifetime reduction due to resonance of electronic transitions with phonons has been observed for several other donors in Si.[6,8,9] In contrast, the phonon density of states at 522 cm^{-1}, half the $1s(A_1)\rightarrow 2p\pm$ frequency, is roughly two orders of magnitude smaller since this frequency is near the phonon cutoff at 526 cm^{-1}, and so the multiphonon decay of the $2p\pm$ state should be much slower. (This second effect, the rapid two-phonon decay of the $2p_0$ state, would also limit the hole burning in the thermal-ionization

model.) The absence of holes in the $2p_0$ transition at low temperatures is most likely a consequence of these differences. The holes which appear at elevated temperature are a consequence of photothermal ionization.

Another important clue to the underlying dynamics behind the hole burning is the result that the burned width (4.6 cm^{-1} FWHM) for $2p\pm$ is much larger than the spectral width of the corresponding infrared region transition in pure Si shown in Fig. 1(a). Because of this discrepancy it is very unlikely that the hole-burning signature is revealing the homogeneous width. Possible hole-broadening mechanisms are as follows: (1) power broadening by the CO_2 laser beam, (2) excited-state splitting caused by alloy inhomogenieties, and (3) spectral diffusion produced by resonant excitation transfer.

Mechanism (1) is not important at the present pump intensity of ≤ 1 W/cm^2 since the transient saturation experiment for this same transition has demonstrated that the saturation threshold is ~ 100 kW/cm^2.

Mechanism (2) can be excluded because the hole-burning experiment has been carried out in the configuration in which the SDL and pump are polarized parallel to the same [100] axis. In this configuration only the p states with [100]-directed orbital motion can be optically excited.

Mechanism (3), spectral diffusion, can account for the observed results and our concentration-dependence studies show that resonant transfer is important. The observed linewidths of the $2p\pm$ and $2p_0$ lines for the S-D center in pure Si depend on its concentration but are nearly independent of the density of other coexisting centers, e. g., S_2, from sample to sample, indicating that resonant transfer controls the linewidth.

In conclusion, persistent spectral holes have been observed for S-H and S-D centers in a Si:Ge alloy by combining a CO_2 pump with an SDL or FTIR probe beam. The alloy sample ensures than an inhomogeneously broadened transition is being probed. The observation that the hole width for the $2p\pm$ transition is wider than the linewidth for the corresponding center in pure Si is ascribed to spectral diffusion produced by resonant excitation transfer. It is also proposed that this same mechanism promotes the electrons from their localized excited states into the conduction band. Electron migration to shallow traps accounts for the observed persistence.

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