Thermal Activation of Valley-Orbit States of Neutral Magnesium in Silicon

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Interstitial magnesium acts as a moderately deep double donor in silicon, and is relatively easily introduced by diffusion. Unlike the case of the chalcogen double donors, parameters of the even-parity valley-orbit excited states $1s(T_2)$ and $1s(E)$ have remained elusive. Here we report on further study of these states in neutral magnesium through temperature dependence absorption measurements. The results demonstrate thermal activation from the ground state $1s(A_1)$ to the valley-orbit states, as observed by transitions from the thermally populated levels to the odd-parity states $2p_0$ and $2p_\pm$. Analysis of the data makes it possible to determine the thermal activation energies of transitions from the donor ground state to $1s(T_2)$ and $1s(E)$ levels, as well as the binding energies of an electron with the valley-orbit excited states.

Keywords: magnesium impurity in silicon, deep center, optical spectroscopy.

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1. Introduction

Interstitial magnesium (Mg_i) in silicon is a deep double-donor defect that has been the subject of several past investigations [1–7] that have uncovered many features of the neutral (Mg_i^0) and singly ionized (Mg_i^+) species. Recent investigations [8,9] have provided more detail and revealed new complexity, including information about complexes Mg forms with other defects. Mg incorporates into Si primarily as an interstitial defect with the ionization energy of about 107 meV in the neutral state, and inhabits the tetrahedral (T_d) interstitial [1,2]. Relative to many single and double donor impurities in Si, such as the Group-V shallow single donors and Group-VI deep donors, the moderately deep double-donor Mg_i center has not been studied as comprehensively. While the transitions to its odd-parity excited states have been studied in some detail, there have been relatively few investigations of the even-parity excited states. A thorough understanding of the electronic structure of Mg_i may prove important in the design of semiconductor lasers using intracenter electronic transitions [10–12]. Transitions to even-parity excited states in particular are important to a complete understanding of cascade relaxation processes [13]. In such processes, electrons are initially captured by highly-excited states and slowly diffuse to the impurity ground state through the ladder of available energy levels, while non-radiative transitions between even-parity states dominate the relaxation.

A proposal in [14] has recently suggested the use of deep donor centers in silicon (Si) as the basis for a new spin qubit-photonic cavity technology. The proposed technology relies on transitions from the ground state to the valley-orbit level $1s(T_2)$ that are forbidden within the effective mass theory (EMT) approximation. These transitions can be very strong for exceptionally deep donors such as the chalcogens [15,16]; however, no sign of these levels has been seen in absorption for Mg in Si until very recently [10]. Mg is a double donor intermediate in depth between the shallow donors of Group-V and the deep-double donors of Group-VI. It may therefore lack the exceptionally strong central cell potential that allows for EMT-forbidden optical transitions between even-parity $1s(A_1)$ and $1s(T_2)$ states. In addition, electronic dipole transitions between $1s(A_1)$ and $1s(E)$ are forbidden by parity, though potentially visible in Raman scattering. However, previous experiments have not revealed the presence of such transitions in Raman spectra of Si : Mg samples [8].

Electronic transitions involving valley-orbit-split (VOS) excited states have been studied in past investigations of shallow donors like substitutional P, As, Sb, and Bi, and interstitial Li and (Li, O). Note that the $1s(T_2)$ state of interstitial Li in Si is downshifted relative to the $1s(A_1)$ state [15], which distinguishes this donor from those with

the substitutional tetrahedral (T_d) symmetry. By thermally populating the $1s(E)$ and $1s(T_2)$ states of the Group-V donors, the authors were able to observe absorption transitions to higher hydrogenic states such as $2p_0$ and $2p_\pm$ [17]. The transitions from the VOS states occur in the infrared absorption spectra at elevated (relative to cryogenic ~ 5 K) temperatures due to thermal population of the VOS donor states, in the temperature range between 20 and 200 K with corresponding maximal intensities at ~ 35 K (VOS = 9.93 meV) to 120 K (VOS = 41.09 meV) [10]. This technique is of course not viable for studies of very deep donors where higher temperatures will result in thermal activation of the final, odd-parity states, $2p_0$ (binding energy is about 11 meV) and $2p_\pm$ (about 6 meV), and it is suggested [10] that, as the shallowest of the deep donors, Mg_i^0 may be close to the limit of its viability. In the case of stimulated emission in silicon intracenter lasers [18], the binding energies of the VOS states can be determined from the lasing transitions terminating at the $1s(E)$ and $1s(T_2)$ states [10]. In this particular case, thermally induced shifts of the donor transitions are excluded.

Preliminary results discussed in [10] have suggested binding energies of 47.4(1) and 49.9(2) meV for the $1s(T_2)$ and $1s(E)$ levels of Mg_i^0, respectively, by observing weak transitions between these levels and $2p_\pm$. An additional estimate [10] was calculated from the absorption spectra of Si : Mg samples subjected to a uniaxial strain. These measurements suggested a binding energy for $1s(T_2)$ of 49.8(1) meV in the unstrained sample. The earlier work [2] established an empirical estimate of the $1s(A_1)$ and $1s(E)$ transition energy for Si : Mg of 56.24 meV based on piezospectroscopic measurements. Binding energies determined in this work and in [10] are somewhat lower than this value. Exceptionally deep donors, e.g., S, Se, or Te, are known to have even smaller $1s(E)$ binding energies of ~ 31 meV meaning their 1s valley-orbit states are more hydrogen-like than helium-like. As the shallowest known isolated double donor, Mg is thought to be more helium-like than the deeper double donor impurities. As such, its somewhat deeper binding energies of the $1s(T_2)$ and $1s(E)$ valley-orbit excited states relative to S, Se, and Te, closer to the estimate of [2], are not unexpected. In this study, we elaborate on [10], demonstrating that the valley-orbit states $1s(T_2)$ and $1s(E)$ of Mg_i^0 can indeed be thermally populated, leading to clearly resolved transitions from both valley-orbit states to the odd-parity states $2p_0$ and $2p_\pm$.

2. Materials and methods

In this study, we measure the absorption spectra of a float zone grown Si sample diffused with Mg. Parameters for Si : Mg sample preparation have been discussed in detail [19,20]. Here, we work with a lightly compensated Si sample with a boron concentration of approximately $1 \cdot 10^{13}$ cm^{-3}, corresponding to the ^{nat}Si low-boron (LB) sample studied in our previous work [8].

This sample was not selected for maximum Mg_i^0 concentration as was done in the preliminary [10] study, but rather for the highest ratio of the desired Mg_i^0 absorption as compared to other absorption transitions in the 30 to 45 meV region. Many weak transitions in this region are as-yet unidentified, and can obscure the relatively weak transitions of interest.

All absorption measurements were performed using a Bruker IFS 125HR Fourier transform infrared (FTIR) spectrometer. A coated Mylar beam-splitter was used, along with a 4.2 K silicon bolometer with an 800 cm^{-1} low-pass cold filter. Samples were mounted on a temperature-regulated stage inside a liquid helium cryostat with polypropylene windows.

3. Experimental results and discussion

In Fig. 1, we see thermally-induced absorbance of the sample in the temperature range of $\sim 70-160$ K.

To clearly observe transitions between the valley-orbit excited states and the higher-lying odd-parity states $2p_0$ and $2p_\pm$, some processing was necessary to remove an absorption feature related to $TO_X - TA_X$ phonon band in Si. This was noted experimentally at 39.04 meV and predicted theoretically at 38.79 meV in [21]. Removal of this feature

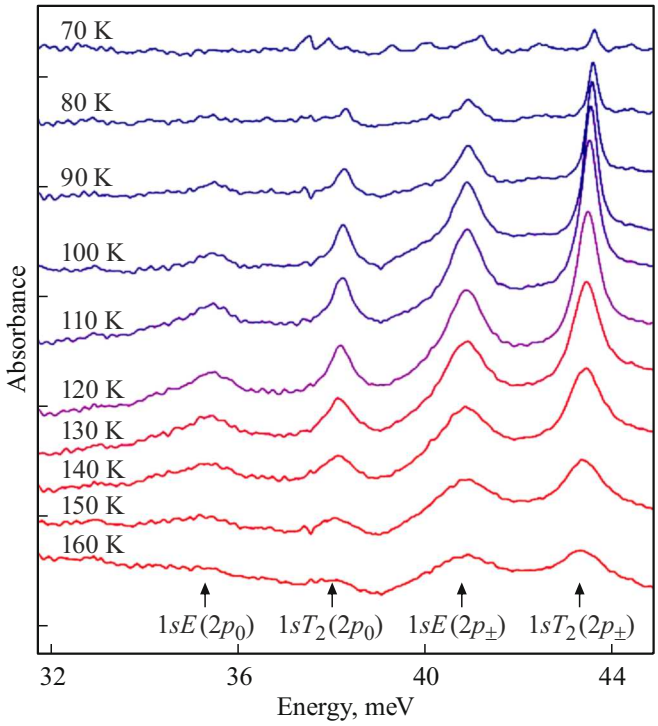

Figure 1. Absorbance spectra of Mg_i^0 over a range of temperatures. As the temperature increases, we see transitions from the thermally populated $1s(T_2)$ and $1s(E)$ levels to $2p_\pm$, corresponding to the higher-energy pair of peaks and to $2p_0$, corresponding to the lower-energy pair. The spectra were obtained at a resolution of 0.5 cm^{-1} (~ 0.062 meV).

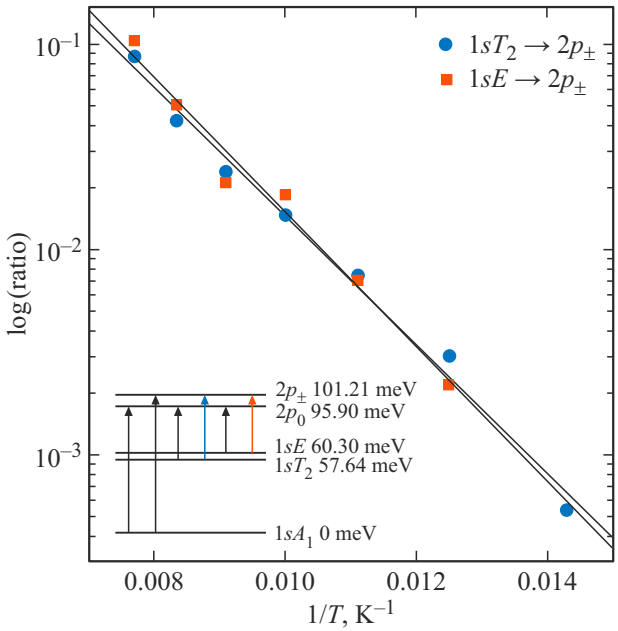

Figure 2. Arrhenius plots corresponding to transitions from thermally populated valley-orbit states $1s(T_2)$ and $1s(E)$ to $2p_\pm$. The areas of the $1s(T_2)$ and $1s(E)$ absorbance features are normalized by the area of the $2p_0$ absorbance at each temperature. The activation energies extracted from the slopes of these plots are 62.3 and 65.2 meV, corresponding to transitions from $1s(T_2)$ and $1s(E)$, respectively. A level diagram displaying these transitions is included as an inset. Indicated optical spacings relative to the ground state $1s(A_1)$ at 0 meV are given as measured at 100 K.

was accomplished by subtracting the appropriate absorbance spectra that were taken using ultrahigh purity (UHP) non-doped Si at each temperature seen in Fig. 1.

With an increase in the crystal temperature, absorption lines appear in the spectra. In addition to the data obtained in [10], the used method allows us to observe transitions from the thermally populated valley-orbit states $1s(T_2)$, and $1s(E)$ not only to $2p_\pm$ states, but also to $2p_0$ levels that are characterized by weaker lines. Taking into account that the binding energies of $2p_\pm$ and $2p_0$ states are 6.38 and 11.7 meV, respectively [2], we estimate the binding energies of the valley-orbit ground states of the neutral double donor as 49.9 meV ($1s(T_2)$) and 47.3 meV ($1s(E)$). These values are in excellent agreement with the preliminary results of [10].

The integrated intensities of curve fits to the peaks in Fig. 1 are displayed as a function of inverse temperature in the Arrhenius plots shown in Fig. 2, normalized at each temperature by the area of the $2p_0$ transition.

These Arrhenius curves correspond to the strongest pair of peaks seen in Fig. 1, namely, transitions from $1s(T_2)$ and $1s(E)$ to $2p_\pm$. From their slopes, we extract activation energies of 62.3 and 65.2 meV for the $1s(T_2)$ and $1s(E)$ transitions to $2p_\pm$, respectively. We note that these are both slightly higher than the optical spacings, which place $1s(T_2)$ and $1s(E)$ states at 57.64 and 60.30 meV, respectively. The result is obtained by subtracting observed binding energies of valley-orbit states from the Mg_i^0 ionization potential of 107.50 meV [2], which is defined at the liquid helium temperature. The small disagreement in positions of thus determined VOS states above the ground state likely results from our inability to measure the sample temperature directly for temperature above 4.2 K.

Finally, we note that there were no signs of similar thermal activation of the valley-orbit excited states for the singly ionized species Mg_i^+. This is not unexpected, since the energy differences between $1s(A_1)$ and $1s(T_2)/1s(E)$ for the singly ionized species is considerably larger than for Mg_i^0. Given the 256.49-meV binding energy of the Mg_i^+ ground state [3], EMT calculations of valley-orbit excited state binding energies for double donors of [22] suggest spacings of 101.49 meV (126.49 meV) between $1s(A_1)$ and $1s(T_2)/1s(E)$ for Mg_i^+.

Conclusion

Expanding upon the results of [10], we have demonstrated clear evidence of thermal activation to the valley-orbit levels $1s(T_2)$ and $1s(E)$, leading to optical transitions to both the $2p_0$ and $2p_\pm$ excited states of Mg_i^0. Within a small constant offset, the activation energies extracted from Arrhenius plots associated with the $1s(T_2)$ and $1s(E)$ to $2p_\pm$ transitions are noted to agree well with the observed optical spacings. No signs of similar transitions from the $1s(T_2)$ and $1s(E)$ valley-orbit excited states of Mg_i^+ could be observed.

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Conflict of interests

The authors declare that they have no conflict of interest.

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