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Shallow donor complexes formed by pairing of double-donor magnesium with group-III acceptors in silicon

R. J. S. Abraham,[1] V. B. Shuman,[2] L. M. Portsel,[2] A. N. Lodygin,[2] Yu. A. Astrov,[2] N. V. Abrosimov,[3] S. G. Pavlov,[4] H.-W. Hübers,[4,5] S. Simmons,[1] and M. L. W. Thewalt[1,*]

[1] *Department of Physics, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6*
[2] *Ioffe Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia*
[3] *Leibniz-Institut für Kristallzüchtung (IKZ), 12489 Berlin, Germany*
[4] *Institute of Optical Sensor Systems, German Aerospace Center (DLR), 12489 Berlin, Germany*
[5] *Department of Physics, Humboldt Universität zu Berlin, 12489 Berlin, Germany*

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Magnesium in silicon primarily occupies an interstitial site, where it acts as a moderately deep double donor. It has recently been shown that interstitial magnesium can pair with the substitutional acceptor boron to form a shallow single-donor center. In this work, we demonstrate analogous complexing with the other group-III acceptors Ga, In, and Al. We observe the odd-parity excited states of each shallow donor complex in absorption spectra, from which the ionization energies are obtained. These complexes can localize excitons, and we observe the donor bound exciton transitions of all four centers in photoluminescence spectra. The Mg-acceptor complexes are found to obey Haynes rule, which predicts a linear relationship between donor ionization energy and donor bound exciton localization energy.

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I. INTRODUCTION

Group-II impurity magnesium, like the group-VI chalcogens, behaves as a helium-like deep double donor in silicon, since magnesium primarily occupies the tetrahedral interstitial site (Mg_i), while the chalcogens occupy the substitutional site [1,2]. Other impurities having two valence electrons, such as Zn and Be, primarily occupy substitutional sites in Si and hence act as double acceptors [3–5]. Mg in Si, while less well studied than the chalcogens, has been the subject of several investigations that uncovered many absorption features of the neutral (Mg_i^0) and singly ionized (Mg_i^+) species [1,2,6–10].

Our recent studies of Mg_i in silicon uncovered several unusual features and clarified a number of outstanding details regarding the electronic structure of this and other Mg-related defects [11,12]. These studies included observation of a perturbed Mg-related double-donor impurity we labeled Mg_{i*}, which likely results from a complex Mg forms with some other impurity or defect [11]. We also observed a shallow donor center whose presence was first noted by Pajot [13]. Those authors observed this center in Mg-diffused silicon and speculated that it might be due to either a Mg-B or Mg-O pair defect. Mg-O pairs were later found to form double donors with ionization energies different from those of isolated Mg_i [7]. Our work identified the shallow donor observed by Pajot [13] as a Mg-B pair, with an ionization energy of 47.50 meV [11]. We also found that the Mg-B complex can bind excitons, as indicated in photoluminescence (PL) spectra by the presence of its donor bound exciton (BE) no-phonon (NP) line and transverse optic (TO) and transverse acoustic (TA) phonon replicas. Furthermore, based on the values inferred from our data for the ionization energy of the donor and its BE localization energy, we demonstrated that the Mg-B donor obeys Haynes rule for shallow donors in Si. This semiempirical relation, first discussed by Haynes [14], predicts a linear relationship between the ground-state ionization energy of a shallow donor or acceptor and the localization energy of its associated BE.

Other studies of Mg-diffused Si carried out by Lin [15] demonstrated the presence of several donor levels beyond those of the Mg_i^0 and Mg_i^+ species. These were noted as having ionization energies of 40, 55, 80, and 93 meV. Lin suggested that some of these levels might arise from Mg-related complexes formed with other impurities such as rapidly diffusing transition metals, or from Mg inhabiting an alternate interstitial site other than the usual T_d.

In this work, we study Mg-diffused Si samples compensated with a variety of group-III acceptors including Ga, In, and Al, as well as the previously studied B. In the infrared region, absorption spectra of the relevant samples reveal evidence of Mg-Ga, Mg-In, Mg-Al, and Mg-B complexes, with excited-state structures essentially identical to those of the group-V shallow donors. In PL spectra, we note the presence of NP lines corresponding to donor BE transitions involving each of these Mg-acceptor pair centers, together with acceptor BE lines associated with the relevant acceptor species. The association between the centers giving rise to the donorlike midinfrared absorption features, and the shallow donor BE transitions, is supported by the excellent correlation between the donor ionization energy and the corresponding BE localization energy for all four Mg-acceptor species [14].

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[*] Corresponding author: thewalt@sfu.ca

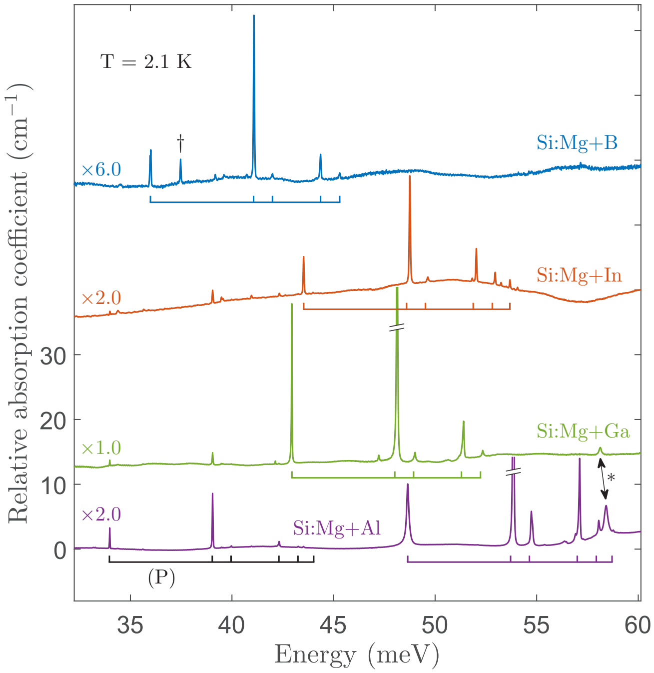

FIG. 1. Infrared absorption spectra showing the donor signatures of Mg-Al, Mg-Ga, and Mg-In complexes, as well as that of unintentional P impurities, and the previously studied Mg-B complex [11]. Arbitrary horizontal shifts are introduced for ease of visibility. For each spectrum in order from lowest to highest energy, the positions of $2p_0$, $2p_\pm$, $3p_0$, $3p_\pm$, $4p_\pm$, and where applicable, $5p_\pm$ transitions are indicated by vertical tick marks. The $2p_\pm$ transitions of Mg-Al and Mg-Ga are truncated, since the sample transmission at the peak went essentially to zero. The features labeled with an asterisk ($*$) are lines 1 and 2 of the Ga and Al acceptor absorption spectra, respsectively. The dagger (†) labels the $2p_\pm$ transition of a potentially Mg-related center, noted in previous work [11]. Spectra were collected at $T = 2.1$ K with 0.1 cm^{-1} (~0.012 meV) resolution.

TABLE I. Energies of the donor absorption transitions shown in Fig. 1. Also given is the extrapolated donor ionization energy, E_i, of each Mg-acceptor pair, and the ionization energy of each acceptor species involved in these pairs, A^0E_i [18].

	Transition energy (meV)			
Label	Mg-B	Mg-Al	Mg-Ga	Mg-In
$2p_0$	35.97	48.65	42.95	43.53
	36.01			
$2p_\pm$	41.08	53.85	48.13	48.76
$3p_0$	41.99	54.73	49.00	49.64
$3p_\pm$	44.36	57.12	51.39	52.03
$4p_\pm$	45.30	58.06	52.35	52.95
$4f_\pm$				53.25
$5f_0$				53.50
$5p_\pm$		58.71		53.68
$5f_\pm$				53.88
$6p_\pm$				54.06
E_i	47.48	60.24	54.51	55.15
A^0E_i	45.63	70.36	74.04	156.90

II. MATERIALS AND METHODS

Results published by Shuman [16,17] include detailed discussion of methods and parameters for Mg diffusion into Si. In this study, we examine spectra from float-zone grown Mg-diffused samples. These included natural Si samples doped with either Al, Ga, or In, with acceptor [Al] and [Ga] concentrations of $\sim 10^{15}$ cm^{-3} and [In] $\sim 5 \times 10^{13}$ cm^{-3}. Additionally, data from our previous investigations in B-containing Mg-diffused Si are included here for comparison. The Mg-B absorption spectrum shown here corresponds to the natural Si low-boron-content sample, with [B] $\sim 1 \times 10^{13}$ cm^{-3}, and the Mg-B PL spectrum to the natural Si high-boron-content sample, with [B] $\sim 2.2 \times 10^{15}$ cm^{-3}, used in our previous work and labeled LB and HB, respectively [11]. All absorption and PL measurements were performed using a Bruker IFS 125HR Fourier transform infrared (FTIR) spectrometer. Samples were immersed in liquid He in cryostats with polypropylene windows for the infrared absorption measurements and fused silica windows for the PL measurements. Sub-λ temperatures were used for all absorption measurements and PL measurements, unless otherwise noted. For infrared absorption spectra, a coated Mylar beam splitter was used, along with a 4.2 K silicon bolometer having an 800 cm^{-1} low-pass cold filter. For PL spectra, a CaF$_2$ beam splitter was used, and PL was generated using ~200 mW of light at either 532 or 1047 nm. The two excitation wavelengths produced similar PL spectra, with 1047 nm light tending to produce less PL from bound multiexciton complexes (BMECs). PL was detected with a liquid-nitrogen-cooled germanium photodiode detector.

All infrared absorption experiments were performed with above-band-gap light incident on the sample, in order to photoneutralize most of the ionized donors and acceptors. This photoneutralization has two effects: First, it reveals absorption due to acceptor species which would otherwise all be ionized in these *n*-type samples. Second, it greatly reduces Stark broadening due to the random electric fields produced by the ionized impurities, resulting in narrower linewidths and revealing higher excited states than would be observed without photoneutralization. Strong photoneutralization is inherent with the above-gap excitation used for the PL measurements.

III. EXPERIMENTAL RESULTS

As seen in Fig. 1, midinfrared absorption spectra of these samples reveal the ground-state to odd-parity excited-state transitions of a number of different species. Readily identifiable are the transitions due to residual P donor impurities, which are present to some extent in all samples, but particularly in the Mg-Al sample. Phosphorus has very well-known transition energies [18] in Si, and the P excited states involved in these transitions are indicated by a bar and tick marks labeled (P) under the Mg-Al spectrum, with the tick marks showing these energies for transitions to $2p_0$, $2p_\pm$, $3p_0$, $3p_\pm$, $4p_\pm$, and $5p_\pm$ states, in order of increasing transition energy.

The binding energies of the odd-parity donor excited states are not significantly affected by the chemical nature of the

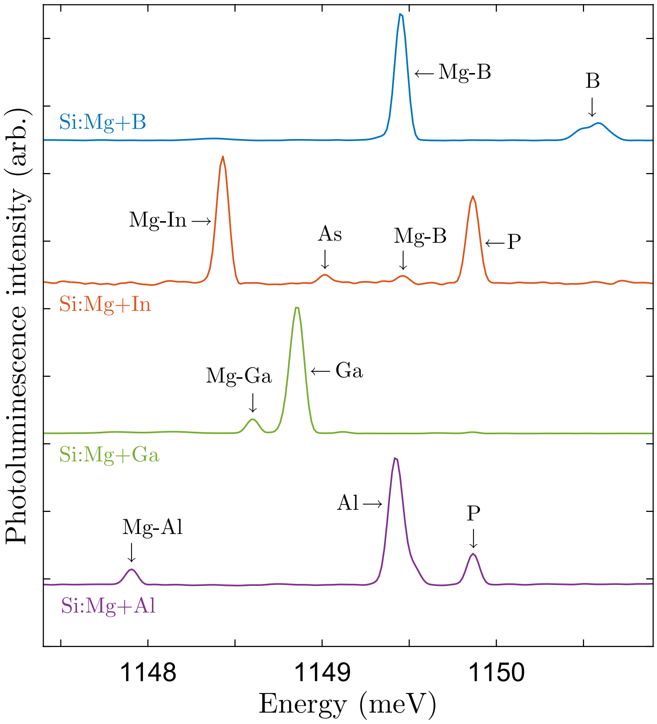

FIG. 2. Photoluminescence spectra showing the NP regions of our Mg-diffused samples compensated with Ga, In, Al, and B. The NP donor BE transitions of the donor complexes, Mg-Al, Mg-B, Mg-Ga, and Mg-In are identified. These appear alongside the NP transitions of several already-known donor and acceptor species, including P, As, Ga, Al, and B. Spectra corresponding to Mg-Al, Mg-Ga, and Mg-In were collected at $T = 1.4$ K, while the sample corresponding to Mg-B was taken at $T = 4.2$ K. All spectra have been normalized to the same maximum height. Scans were collected at a resolution of 0.5 cm^{-1} (∼0.062 meV).

donor species, unlike the even-parity ground state, which is responsible for the chemical shift in donor ionization energy, so the same bracket used to label the P transitions can be shifted in energy to identify transitions arising from other shallow donor species, as shown for the Mg-Al, Mg-Ga, Mg-In, and Mg-B donor complexes. The spectra in Fig. 1 also reveal acceptor transitions arising from remaining unpaired Al and Ga acceptor impurities in those two samples. The absence of absorption from the B acceptor likely results from the much lower B concentration as compared to the samples doped with Al or Ga. Absorption from the In acceptor occurs in a different, higher energy spectral region, which was not investigated. A line thought to be the $2p_{\pm}$ transition of an unidentified, possibly Mg-related, shallow donor has been reported before [11], and is labeled with a dagger (†) in the spectrum of the Mg-B sample in Fig. 1.

The energies of all observed shallow donor absorption transitions arising from Mg-acceptor pair centers are given in Table I, along with the ionization energy, E_i, for each species, which is obtained by adding the energy of the $3p_{\pm}$ transition observed for a given species to the theoretical effective mass binding energy of 3.120 meV for that excited state [18]. Also tabulated is the acceptor ionization energy, A^0E_i, for the acceptor impurity associated with each of these pair centers. As can be seen in Table I, there is no obvious correlation between the ionization energy of a given acceptor and the ionization of the shallow donor which results from pairing that acceptor with Mg_i.

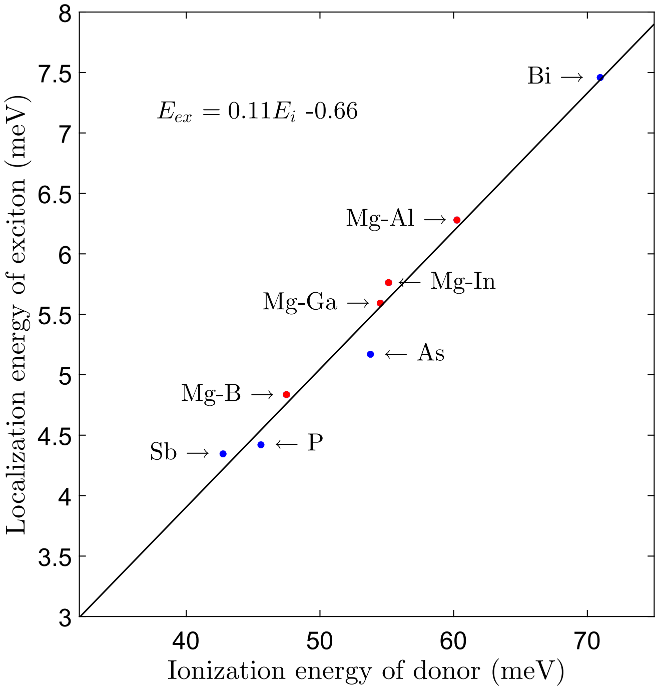

FIG. 3. The bound exciton localization energy E_{ex} for a given donor species plotted against its ground-state ionization energy E_i, demonstrating good agreement with the linear relationship expected from Haynes rule [14].

PL spectra covering the NP region of shallow donor and acceptor BE of the four samples containing Mg_i and either B, Al, Ga, or In are shown in Fig. 2. The well-known NP transitions of excitons bound to the donors P and As, which are unintentional impurities in these samples, and the acceptors B, Al, and Ga are readily identified. Note that the In BE NP line occurs at ∼1140.9 meV, and while it was indeed observed in the PL spectrum of the Mg-In sample, it lies well outside the spectral range shown in Fig. 2. Four other BE NP lines are observed, one of which has been previously [11] identified as a shallow donor BE transition resulting from Mg-B pairs. We similarly identify the other three new BE NP lines shown in Fig. 2 as being shallow donor BE transitions arising from the analogous Mg-Al, Mg-Ga, and Mg-In pairs. We note in Fig. 2 that a small amount of the NP line of the Mg-B complex is visible in the PL spectrum of the In-compensated sample, which results from the presence of unintentional B in that sample.

As shown in Fig. 3, these identifications are strongly supported by the fact that all four Mg-acceptor shallow donor complexes closely follow Haynes rule [14], which posits a linear relationship between shallow impurity ionization energy, E_i, and the localization energy of excitons bound to that impurity, E_{ex}. The ionization energies are as given in Table I, and the bound exciton localization energies are measured relative to that of the P bound exciton, which is taken to be

4.42 meV as measured by the energy difference between the P TA phonon replica PL line and the low-energy edge of the free exciton TA phonon replica PL. The best fit to the data shown in Fig. 3 gives the Haynes rule result for shallow donors in Si to be $E_{\text{ex}} = 0.11E_i - 0.66$ meV.

IV. DISCUSSION AND CONCLUSION

The results presented here verify our earlier conjecture [11], based on the results for Si containing both B and Mg_i, that interstitial Mg might complex with all Group-III acceptors in Si to form unique shallow donor centers. This result is readily understood, since there is an electrostatic attraction between an ionized Group-III acceptor, in the -1 charge state, and an ionized Mg_i double donor in the $+2$ charge state, and the relatively large low-temperature mobility of species diffusing interstitially allows for the formation of pairs which minimizes the electrostatic potential energy. The single-donor nature of the pair results from the $+3$ valence of the acceptor combining with the $+2$ valence of the Mg_i to give a net valence of $+5$, as for the Group-V shallow donors. A calculation of the expected donor binding energies of these complexes using pseudopotentials for the Group-III acceptor and the Mg_i would be an interesting theoretical problem.

It would be interesting to search for other complexes which might be formed by the diffusion of Mg_i into Si. A very well-known isoelectronic bound exciton (IBE) producing very strong PL in Si is formed by the pairing of Be_s with Be_i [19], and in analogy a Mg_s-Mg_i IBE has recently been identified by its isotopic fingerprint in ^{28}Si [12]. One might expect new IBEs, perhaps with interesting properties, to be formed by pairing between the known substitutional double acceptors Be_s and Zn_s with Mg_i.

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