Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

Magnesium-related shallow donor centers in silicon

S.G. Pavlov [a,*], Yu.A. Astrov [b], L.M. Portsel [b], V.B. Shuman [b], A.N. Lodygin [b], N.V. Abrosimov [c], H.-W. Hübers [a,d]

[a] *Institute of Optical Sensor Systems, German Aerospace Center (DLR), Berlin, Germany*
[b] *Ioffe Institute, Russian Academy of Sciences, St. Petersburg, Russia*
[c] *Leibniz-Institut für Kristallzüchtung (IKZ), Berlin, Germany*
[d] *Institut für Physik, Humboldt-Universität zu Berlin, Berlin, Germany*

ABSTRACT

Magnesium (Mg) atoms, diffused in silicon (Si) lattice at high temperatures, tend to form specific bonds to host Si atoms, to other Mg atoms as well as to other defects in a Si crystal. These electrically active donors exist either as isolated atomic type centers or as complexes coupling magnesium to other trace elements in silicon. We report on shallow Mg-related donor centers in moderately doped Si:Mg crystals which are distinguished by their infrared absorption spectra. These complexes have energy spectra, relatively dense filling two separated infrared ranges, 30–95 meV and 105–130 meV, having clearly different genesis. These centers are observed in silicon of various purification degree, including high-purity crystals with low oxygen and carbon content. We assign the formation of such localized states in Si:Mg to electrically active donor complexes with different numbers of magnesium atoms, similar to those formed by interstitial oxygen in silicon. The results obtained are incorporated into the general phenomenon of formation of shallow donors in silicon which is related to interaction of impurities in the semiconductor.

Subject areas: Semiconductor Physics, Diffusion Doping, Silicon.

1. Introduction

While isolated atomic dopants, forming electrically active impurity centers in semiconductors, are well known, complexes which are formed purely by these atoms or by binding to other trace elements are less understood and their origin and properties remain an important area of research. Diatomic donor centers are characteristic for substitutional chalcogens in silicon: selenium (Se), sulfur (S), tellurium (Te) [1]. They can be formed by pairing the same chalcogen atoms (Se_2, S_2, Te_2) as well by combinations (Se + S, S + Te, etc) [2]. For interstitial atoms, pairing to residual and trace elements in the host lattice dominates. In the case of silicon, shallow impurity-related complexes have been found for interstitial oxygen, its pairs with lithium, nitrogen, and carbon as well as for hydrogen-induced donors [3–10]. Since these supplementary impurities can affect various properties of semiconducting devices, from their electric conductivity to radiation hardness, knowledge of their formation, passivation and physical properties is one of the key elements in semiconductor physics and technology.

Magnesium atoms (group-IIA) as isolated donor centers have binding energies between those of shallow donors from group-V elements (such as phosphorus), and the deeper chalcogen donors from group-VI (S, Se, Te). They may open potential n-Si applications in the mid-infrared wavelength range, for instance as broad-band infrared detectors or as mid-infrared emitting sources [11]. Since both applications depend critically on the full spectrum of electrically active donors, especially on those with a smaller activation energy, knowledge on the energy spectra and on the origin of shallow Mg-related complexes is crucial.

Recent technological progress in doping of silicon (Si) with magnesium (Mg) by a diffusion technique [12,13] provided high quality, research grade Si:Mg crystals and enabled a series of important scientific results on the structure of isolated Mg donors and its complexes with other defects in the lattice [11,14–16]. Isolated magnesium atoms (group-IIA) in silicon have been shown to form double donor centers in different charge states: as a neutral Mg^0 with a binding energy $E_{Mg0} =$ 107.51 meV and as a singly ionized Mg^+ with a binding energy $E_{Mg+} =$ 256.68 meV [17]. A few Mg-related donor complexes formed by pairing of Mg with another atom(s) X, D (Mg, X), become detectable in infrared (IR) absorption spectra at moderate Mg concentrations and/or moderate

---

* Corresponding author.
  E-mail address: sergeij.pavlov@dlr.de (S.G. Pavlov).

concentrations of other elements, such as interstitial oxygen (X is oxygen atom, O), with the binding energy $E_{Mg,O} = 124.66$ meV [18] or substitutional acceptors of group III atoms (X ≡ Al, B, In, Ga), with the binding energy $E_{Mg,A}$ in the range 47–55 meV [16]. A new Mg-related center, Mg* (not yet assigned X), with the binding energy $E_{Mg*} = 94.4$ meV has been observed in IR spectra [14]. Until now, the exact structure of these centers is not known.

We report on a series of impurity transitions observed in IR absorption spectra of float zone (FZ) grown Si crystals, which are diffusion-doped by Mg. Spectral lines in the range around 30–95 meV, below those of the isolated Mg^0, occur in the specially purified crystals with low trace/residual donor and acceptor concentrations in the range of $(1–5) \times 10^{12}$ cm^{-3}. We assign such donors to Mg clusters with different numbers of bound Mg atoms and will refer to these shallow donors as D_n (Mg). The series of the lines corresponding to donors, whose binding energies (between 117 meV and 133 meV) exceed that of the isolated neutral Mg^0 donor, occur in the Si:Mg samples after their storage at room temperature with typical formation times up to several months and longer. These deeper centers are probably formed due to Mg atoms binding to oxygen point defects in Si. We shall call them "evolving" donors, ED_n (Mg). Part of them was found in IR absorption spectra of the pure (nominally oxygen-free[1]) Si:Mg samples, while others appear in conventional (not specially purified) FZ Si crystals. The diversity of observed Mg-related donors in silicon is similar to the well-established formation of variety of so-called thermal donors (TDs) in Si, which can be thermally-activated in oxygen-rich[2] (from 10^{16} cm^3) Si [2–4].

2. Experimental details

2.1. Sample preparation

This study summarizes the experimental results obtained by sequential measurements over the past eight years of about 20 samples prepared in different ways, from about 50 silicon samples doped by magnesium. By this way, links were investigated between the formed shallow Mg donor complexes (some of them do not appear in all investigated samples) and the impurity content in the original Si crystals as well as to the technological treatment. Also, the long-time evolution and stability of the complexes were studied.

The initial Si crystals were float zone grown. Typically, Si wafers with a diameter of 30 mm and a thickness of 2 mm were used for doping with magnesium. Most of the experiments were done using Si:Mg samples obtained from high-purity n- and p-type Si crystals with residual concentrations of oxygen and carbon of $\sim1 \times 10^{14}$ cm^{-3} and $\sim1 \times 10^{15}$ cm^{-3}, respectively (samples from specially purified crystals, Table 1.). Such pure crystals were grown by applying a purification technology developed in the Avogadro project to obtain isotopically enriched high-purity monocrystalline Si [19]. These samples had low concentrations of residual shallow donors and acceptors in the range $5–65 \times 10^{11}$ cm^{-3}. The other samples were prepared from conventional FZ p-Si-crystals with an oxygen content of $\sim1 \times 10^{16}$ cm^{-3} and with boron concentrations ranging from residual 4×10^{12} cm^{-3} in the undoped Si up to 8.8×10^{14} cm^{-3} in doped Si.

The doping by Mg was performed by high temperature diffusion using the so-called "sandwich" technique (for more details see Refs. [12, 13]). We used pure magnesium (99.9995–99.9999% as specified by the Mg suppliers) for doping the initial crystals. The depth profiles of the electrically active Mg, measured by the differential conductivity method [12], showed that the $(1/e)$ characteristic length of the Mg

concentration decay in depth is about 600 μm. This is a result of diffusion at a temperature of 1000 °C in the course of 2.5 h, and the following ordinary, slow cooling. This result refers to the case, where only one surface of the wafer served as a source of the impurity. Most of the investigated samples had a final thickness less than 2 mm. To provide a homogenous doping, both surfaces of a 2.0–2.5 mm-thick Si wafer were covered with Mg films by thermal evaporation of the metal in vacuum. Two other Si wafers were attached to both wafer sides, "sandwiching" this sample. The "sandwich" was then loaded into a quartz ampoule. After pumping out the air from the ampoule and filling it with argon, the ampoule was sealed and loaded into a high-temperature oven. From multiple tests done on Mg diffusion in Si, the optimal duration providing maximal concentration of neutral Mg^0 centers was determined to be in the range 2.5–7.5 h at 1100–1250 °C. Immediately after the diffusion, the ampoule was cooled with an air or nitrogen gas flow at room temperature. The typical cooling time until the temperature at which the visible glow of Si disappeared, was $\sim$100 s. If it is not otherwise indicated in the following text, this cooling mode was applied during sample preparation. Two samples (MgQ1, MgQ2) were prepared from the high-purity Si from the wafers of a smaller ($\sim$10 mm) diameter and at a higher post-diffusion cooling rate. For such samples, the ampoule was dropped into mineral oil after the diffusion, which provided a characteristic cooling time of a few seconds only. The high-purity p-Si of the resistivity of 2000 Ω × cm was used as the initial material for these quenched samples.

After cooling, the external Si wafers welded to the sample were mechanically removed by grinding them down, including $\sim$50 μm surface layers of the initial, sandwiched Si wafer. From the remaining $\sim$2 mm thick wafers, Si:Mg samples were prepared for further characterization. Usually, a few samples from each doped wafer were prepared. We note that the parameters of the samples given in Table 1 relate to an individual Si wafer, while determination of Mg-related centers was made over a set of samples prepared from the same wafer: the pieces of a wafer did not always show identical spectral line sets in the infrared absorption spectra.

2.2. Sample characterization

An elemental analysis of a few samples with the Secondary Ion Mass Spectrometry (SIMS) showed a high Mg content in the doped crystals [20], which is about two orders of magnitude larger than the density of Mg^0 centers, as derived from Hall measurements in the temperature range of 78–300 K [21]. This indicates a relatively large content of Mg, presumably in the form of precipitated inclusions of Mg_2Si [22], which are electrically neutral.

Relative and absolute (for the centers with known calibration parameters) abundances of electrically active centers (donors, acceptors) in the investigated Si crystals have been determined from the Hall effect measurements and corresponding intensities of impurity transitions in the low-temperature absorption spectra.

The concentrations of most abundant residual impurities in silicon, which are not electrically active, such as carbon and oxygen, were estimated from the intensities of their specific bands in the infrared spectra. In most of the samples, interstitial oxygen occurred at low concentration. In all samples, prepared from high-purity silicon, no specific spectral features have been observed in the absorption spectra which are either for isolated carbon [23] or for compounds related to oxygen, for instance O-precipitates [24]. This observation holds for original (before diffusion) high-purity Si crystals and Si:Mg (after diffusion) samples. Therefore, we consider their occurrence at low to vanishing concentrations, as expected for float-zone grown high purity crystals. Only interstitial isolated oxygen is considered to take part in the formation of Mg-related donor complexes.

Impurity absorption spectra were measured using a Bruker Vertex 80v Fourier transform IR spectrometer, see for details Ref. [25]. The spectral resolution was varied between 0.085 cm^{-1} and 1 cm^{-1} (photon

---

[1] We point out that in the course of a high-temperature processing of a nominally free-oxygen silicon wafer in a quartz ampoule – see the next Section – a Si:Mg sample is slightly contaminated with oxygen, which vapor is formed due to decomposition of quartz.

[2] Mainly in Czochralski-grown Si.

Table 1

Parameters of Si:Mg samples whose impurity spectra are investigated in the work. (p-), (n-) stand for residual conductivity of undoped initial Si crystals at room temperature; (B) Boron doped p-Si original crystals. Mg* centers are present in all investigated samples. The abundance of D (Mg,X) complexes is determined from all spectra over the measured time elapsed after diffusion; % stands for relatively weak impurity lines, Y indicates a moderate intensity of the intracenter transitions.

Sample No	Original Si: Residual and/or added B impurities, cm^{-3}	Diffusion parameters			Net Mg concentration, N_D-N_A, cm^{-3}	Type of D (Mg,X) complexes		
		temperature	time	Post-diffusion cooling rate		D (Mg,X$\neq$Mg), X $\equiv$	D_n (Mg)	ED_n (Mg)
Undoped FZ-grown Si crystals with low, residual oxygen ($\sim1 \times 10^{16}$ cm^{-3})								
Mg01	(p-) 4.2×10^{12}	1250 °C	25 h	$\sim$100 s	4.7×10^{14}	%O	%	%
Mg02	(p-) 6.5×10^{12}	1200 °C	1.0 h	$\sim$100 s	4.8×10^{14}	%O, Li	%	%
Boron-doped FZ-grown Si crystals with low, residual oxygen ($\sim1 \times 10^{16}$ cm^{-3})								
MgB1	(B) 5.2×10^{14}	1200 °C	2.5 h	$\sim$100 s	7.3×10^{14}	B, O	Y	
MgB2	(B) 4.5×10^{14}	1200 °C	2.0 h	$\sim$100 s	9.7×10^{14}	B, O, Li	Y	%
MgB3	(B) 8.8×10^{14}	1250 °C	2.5 h	$\sim$100 s	2.5×10^{14}	B, O	%	
Specially purified FZ-Si crystals with ultra-low O ($\sim1 \times 10^{14}$ cm^{-3}) and C ($\sim1 \times 10^{15}$ cm^{-3})								
MgP1	(n-) 5.4×10^{11}	1250 °C	7.5 h	$\sim$100 s	1.15×10^{15}	%B, Li	Y	%
MgP2	(n-) 5.4×10^{11}	1250 °C	1.0 h	$\sim$100 s	1.27×10^{15}	%B, Li	Y	Y
MgQ1	(p-) 6.5×10^{12}	1100 °C	2.5 h	a few s	5.8×10^{14}	%B	Y	
MgQ2	(p-) 6.5×10^{12}	1250 °C	2.5 h	a few s	1.82×10^{15}	%B, %O	Y	Y

energy of 10–120 μeV). The diagnostic IR light was focused on a spot of 2.5 mm diameter in the center of a Si:Mg sample.

3. Impurity transitions of Mg-related donors

At low temperature electrons occupy the ground states of the center, and the absorption spectroscopy resolves discrete transitions of bound electrons from the ground into excited states of the center. These transitions are grouped in series often called Lyman series because of their analogy to the transitions of atomic hydrogen. Only dipole-allowed transitions of electrically active donor centers were measured. The low-temperature absorption spectra of the moderately doped Si:Mg samples show intense mid-IR impurity lines of isolated neutral Mg^0 centers and paired (Mg,X$\neq$Mg) complexes as well as series features of shallow Mg-related donors observable in both, far- and mid-IR wavelength ranges (Fig. 1). We observed no indication of shallow donors in the specially prepared test samples made from the same initial high-purity Si crystals under the same procedure, but without using Mg at the high-temperature treatment.

The majority of the observed transitions show spectroscopic patterns very similar to those of the group-V hydrogen-like (H-like) donors. This is apparently due to the strong screening of the extra charge of the impurity core by an inner electron [26] that is in the frame of the effective mass theory (EMT). In this model, all H-like donors in Si have a similar structure of the odd-parity, high excited states, and are characterized by very close values of the corresponding interstate energy spacings and relative line intensities. A necessary, but not sufficient condition for the identifying donors as H-like centers is that experimental intracenter infrared transitions spacings are very close to those predicted by the EMT, independently on the chemical nature of the H-like center. The impurity transition into the $3p_\pm$ state is usually clearly resolved in absorption spectra of donors in silicon and it also can be derived by comparing its energy intervals to the transitions ending in the $2p_0$ state (the lowest photon energy in the IR absorption impurity spectrum, typical H-like center spacing for n-Si is 8.371 ± 0.035 meV) and in the $2p_\pm$ state (the most intense line in the spectrum, typical H-like center spacing for n-Si is 3.281 ± 0.002 meV) [26]. It is common to obtain the electron binding energy of such a donor center (that is, its ionization potential) by adding the transition energy from the ground state to a particular excited state, which is usually the $3p_\pm$ state, assigning its energy to the EMT value of 3.12 meV [27].

3.1. Isolated Mg double donors (Mg^0 and Mg^+)

Transitions related to the isolated neutral Mg^0 state are located in the mid-IR spectral range with photon energies between 95 meV and 107 meV (Fig. 1). Transitions of the isolated magnesium in the single-ionized charge state are in the range above 200 meV. A complete list of the
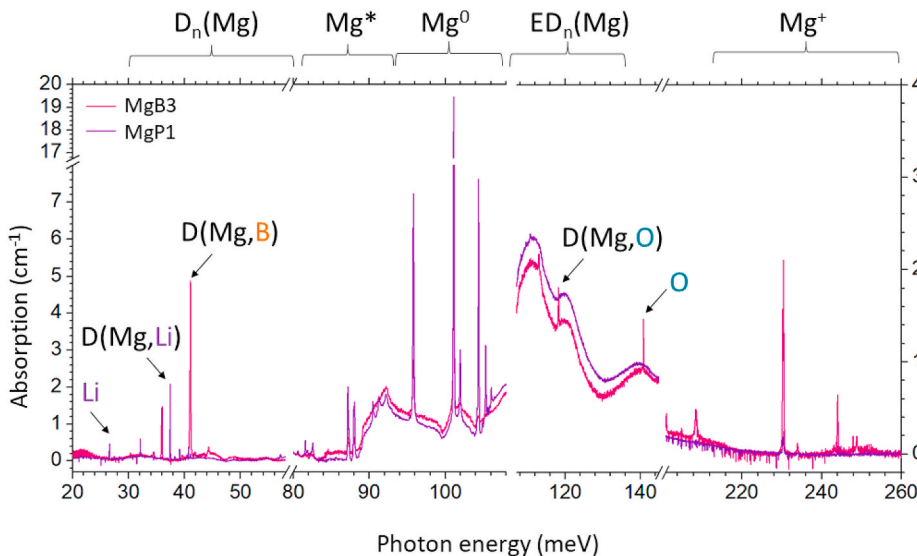

Fig. 1. Typical IR absorption spectra of Si:Mg samples prepared from high-purity n-Si (#MgP1) and conventional boron-doped material (#MgB3) at T ∼ 5 K. Shown on the top are transitions series/classes related to the isolated Mg centers (being in the neutral Mg^0 and charged Mg^+ states) and to Mg-clustered centers (see Sections IIIa-d for details). The transitions related to the centers formed by pairing of Mg with other defects in the crystals, which are residual interstitial oxygen (O), substitutional boron acceptors (B), and interstitial lithium (Li), are marked in the plot. Li stands for the single-donor transitions. O stands for IR-active oxygen vibration modes.

isolated Mg atomic transitions can be found in Ref. [14].

3.2. Mg donors due to coupling with residual interstitial atoms and other substitutional atoms (D (Mg,X))

The pairing of interstitial Mg with other interstitial atoms in the Si lattice forms different types of centers (Table 2), with intracenter transitions falling in the spectral bands below and above those for an isolated Mg^0 center. Typical energy spacing for the D (Mg,X$\neq$Mg) transitions ending in the $\rightarrow 2p_0$ and $\rightarrow 3p_\pm$ states, is within 8.54 ± 0.09 meV, that exceeds those for shallow donors in Si, while it fits well to those between $\rightarrow 2p_\pm$ and $\rightarrow 3p_\pm$ transitions, which is about 3.26 ± 0.02 meV (Table 2).

The pairing Mg with Li atom, having a single electron in the outer shell, results in a D (Mg,Li) center with the binding energy between those for an isolated Li single donor and for an isolated double Mg^0 donor (sample #MgP2, Fig. 2). This center is more shallow than most of isolated group-V substitutional donors in Si [27] and donors formed by Mg-acceptor pairs D (Mg,A_s), where A_s are elements of the group III [16]. In a few Si:Mg samples, the Li-related lines appear in the IR spectra after Mg diffusion, while they are absent in the reference Si samples, when no Mg was present at the high-temperature processing of the sample. Therefore, we explain the lithium-related lines by the presence of the trace Li impurity in the initial Mg. We emphasize that the D (Mg, Li) centers were not observed in samples underwent the rapid post-diffusion cooling (samples MgQ1, MgQ2). This indicates the destructive role of quenching for this most weakly bound D (Mg,X$\neq$Mg) complex.

The pairing to unknown yet atom forms a specific Mg* double donor with a binding energy $E_{Mg*} = 94.4$ meV [14]. This donor has been recently assigned to a Mg complex paired with either another Mg atom (i.e. this forms the diatomic Mg_2) [28] or with a different trace atom D (Mg,X$\neq$Mg) [14]. The main feature making Mg* different from the diatomic double chalcogen substitutional donors S_2 and Se_2 observed in Si [29] is the fine split (less than 1 meV) structure of the ground state, that indicates on its specific symmetry, different from T_d type, common for all other shallow and double donors in Si [14]. The energy spacing between the corresponding transitions ending in the $\rightarrow 2p_\pm$ and $\rightarrow 3p_\pm$ Mg* states follows the common trend for the D (Mg,X$\neq$Mg) pairs, while the spacings between $\rightarrow 2p_0$ and $\rightarrow 2p_\pm$ Mg* transitions exceeds the EMT value.

The pairing Mg with the interstitial O atom, forms a double donor D (Mg,O) [18]. This is the only donor complex with the binding energy ($E_{Mg,O} = 124.67$ meV) exceeding those for an isolated neutral Mg^0. The energy spacings between the mentioned characteristic transition pairs ($\rightarrow 2p_\pm$ and $\rightarrow 3p_\pm$ or $\rightarrow 2p_0$ and $\rightarrow 2p_\pm$) of D (Mg,O) is very close to

Fig. 2. Typical IR absorption spectra of three Si:Mg samples in the far-IR region of D_n (Mg) intracenter transitions. Note the identical, H-like structure (depicted with gray insets) of the impurity spectra related to the D_n (Mg) donors as well as spectra of residual H-like substitutional phosphorus (P), interstitial lithium (Li), D (Li,O) and D (Mg,Li) complexes.

those for a double Mg^0 donor.

In particular cases of low Li and low O in the crystals, only the strongest D (Mg, X) donor related transition(s) are detectable. The intensity of the D (Mg,X) transitions is about an order of magnitude smaller of those in the Mg^0 neutral state.

The pairing of interstitial Mg with substitutional acceptors in the Si lattice (Mg-acceptor pairs D (Mg,A_s)) has been thoroughly studied in Ref. [16]. We note here that the D (Mg,B) center was observed in samples with a very low, residual boron and high concentration of electrically active magnesium.

3.3. Observation of a series of other shallow Mg-related donors (D_n (Mg))

The low-temperature absorption spectra of the moderately doped Si: Mg samples show other Mg-related complexes filling both the far- and mid-IR wavelength ranges. The intensity of these transitions, assigned to the D_n (Mg) and ED_n (Mg) donor centers, is another order of magnitude less than of those for the Mg^0 neutral state, and if compared with those for the D (Mg,X) complexes. The characteristic transitions at the low-energy side in the IR absorption spectra ($E_{Dn} < E_{Mg0}$, Figs. 2 and 3), assigned to the D_n (Mg) donor centers, appear immediately after Mg diffusion which is different for the evolving Mg-related centers discussed below, in Section IIId. To label the D_n (Mg) centers, we follow the conventional for the oxygen-TD_n numbering, namely, starting from those with the largest binding energy (Table 3). It should be noted, that the assignment of numbers n for the D_n (Mg) centers is preliminary. We did not succeed to assign all observed lines to specific centers since many weak lines overlap with other strong impurity lines or because they are hidden in the multiple-phonon absorption bands.

The data in Table 3 are collected from a number of samples. Note, that not all D_n (Mg) donor centers are present in the IR spectra of each sample (see an example of different mid-IR spectra for samples made from the same original high-purity Si crystal, different post-diffusion cooling rates, Fig. 3). For each specific center at least two strongest

Table 2

Intracenter transitions (in meV) of different Mg-related donor complexes formed through Mg interaction with other interstitial atoms, residual O and accompanying the diffusion doping Li, as compared to the Mg* center [14]. The accuracy of the energy values for centers in O-containing Si:Mg as derived from the IR spectra and averaged for the Si:Mg #MgB1,2,3 and #MgQ2 samples is ± 0.005 meV. The accuracy of the energy values for centers in Li-containing Si:Mg derived from the IR spectra of the Si:Mg #MgP1,2 is ± 0.004 meV. The accuracy of the estimated binding energy E_i is ± 0.01 meV. MP stands for the spectrally unresolved multiplet, the MP peak energy is given. The observed intracenter transitions of Mg paired to other interstitial atoms and the derived binding energies for such centers fit well to the data assigned previously to D (Mg,O) [18], to Mg* and not identified complex D (Mg,X) [14].

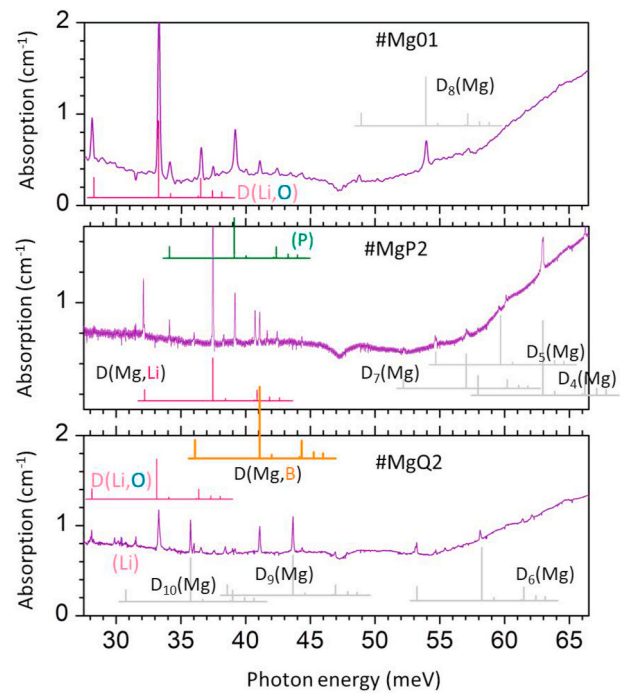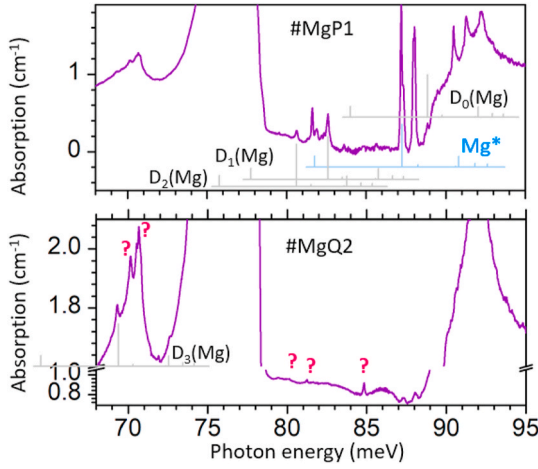| Transition	Next to Mg abandoned interstitial atom in the D (Mg, X) donor complex:		
1s (A₁)$\rightarrow$	Li	Mg	O
$2p_0$	32.107	MP82.57	113.002
$2p_\pm$	37.470	87.98	118.300
		88.06	
$3p_\pm$	40.726	91.28	121.555
		91.31	
E_i (meV)	43.85	94.40	124.67

Fig. 3. Typical low temperature absorption spectra of Si:Mg samples in the mid-IR region (at photon energies close to the Mg* transitions) of the D_n (Mg, X) intracenter transitions. Shown are spectra for two Si:Mg samples made from the same initial high-purity Si crystal. Different post-diffusion first-stage cooling were applied: regular (>100 s) for the sample #MgP1, and rapid (a few seconds) for the sample #MgQ2. Question marks (?) indicate the transitions that are not specified.

characteristic transitions were taken for identification of the center. These are the transitions from the ground state into the $2p_\pm$ and $3p_\pm$ excited states. Many transitions occur as not resolved multiplets that make them similar to those for a Mg* center. Typical energy spacings for the D_n (Mg) donors are about 8.39 ± 0.05 for the transitions terminating in the $2p_0$ and in the $3p_\pm$ states and about 3.287 ± 0.031 meV for the transitions terminating in the $2p_\pm$ and in the $3p_\pm$ states (Table 2), i.e. very close to the EMT [27] and experimental values for the single H-like donors in silicon [26].

The quenching does not destroy the D_n (Mg) donor centers with very low binding energy (Fig. 2), i.e. with an electron weakly bound to a center. This is different from the behaviour of the weakly bound D (Mg, X≠Mg) centers, not surviving rapid cooling rates, see Ref. [15]. In contrast, the rapid cooling modifies significantly the content of D_n (Mg) donor centers with the largest binding energies if compared to the case of samples slowly cooled after diffusion (Fig. 3).

3.4. Evolved Mg-related centers (ED$_n$(Mg))

A few donor intracenter transitions ED_n (Mg) appear in the mid-IR spectral range (Fig. 4) in moderately doped Si:Mg samples after a relatively long (>one year) storage time. Their binding energy exceeds those for the isolated Mg^0 center ($E_{EDn} > E_{Mg0}$). The following main trends were observed in the long-term evolution of most of these relatively deep ED_n (Mg) centers:

(i) In the Si:Mg samples with detectable oxygen (in general the local

O vibration modes are traced in the IR absorption spectra down to an oxygen content of $\sim 10^{16}$ cm^{-3}) absorption at intracenter transitions of D (Mg, O) complexes increases with the time elapsed after the diffusion doping, while the absorption by isolated Mg^0 donors decays with the similar rate. This indicates the direct link between the rise in concentration of the D (Mg, O) centers and migration of interstitial Mg from its isolated positions toward isolated interstitial oxygen atoms that can serve as effective traps of light interstitial atoms (Mg, Li). Other Mg-related centers occur to be stable over the measured time. Thus, D (Mg, O) complexes occur to be the main drain in the process of spatial redistribution of magnesium in a crystal, while neutral Mg^0 centers act as a main source in this process (Mg* centers may be the next, weaker source: their line intensity is usually reduced in the first months following diffusion). These evolving ED_n (Mg) centers exhibit their characteristic lines at photon energies around those of a D (Mg, O) center (Fig. 4 lower graph).

(ii) In Si:Mg samples with a low oxygen content, Mg^0 centers also play the role of a source. At least one new evolving center, ED_3 (Mg), occurs in the IR spectra of such samples (Fig. 4, upper graph), with spectral lines at photon energies between those of the isolated neutral Mg^0 and neutral $(Mg,O)^0$ donors ($E_{Mg0} < E_{EDn} < E_{Mg,O}$).

Typical experimentally determined spacings of transitions into → $2p_\pm$ and → $3p_\pm$ states of the ED_n (Mg) donor centers coincide approximately with the corresponding EMT values for a single H-like donor in silicon while the transitions terminating in the $2p_\pm$ state exhibit a fine splitting similar to those observed in several D_n (Mg) donors, and also in Mg* center. All new evolving centers exhibit the energy structure of odd-party excited states similar to those for the H-like donor in Si (Table 4).
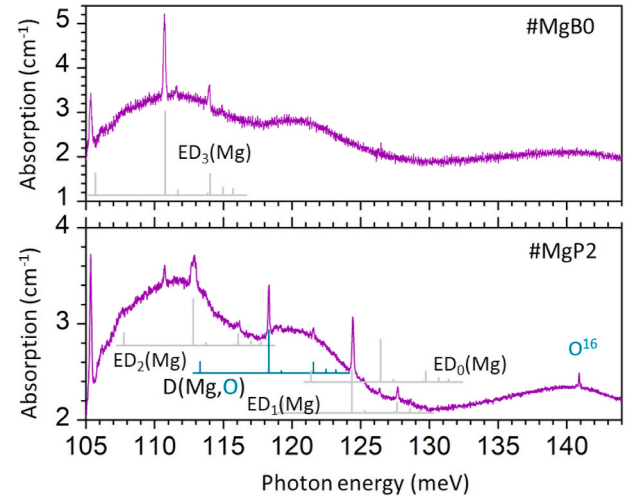

Fig. 4. IR absorption spectra of Si:Mg samples in the mid-IR region which demonstrate ED_n (Mg) intracenter transitions at photon energies above the Mg^0 transitions.

Table 3

Strongest intracenter optical transitions (in meV) of the D_n (Mg) complexes formed on a short time scale (days-weeks). The uncertainty of the transition energies derived from the spectra is ± 0.01 meV. The binding energy of a center is determined by adding 3.12 meV to the energy of the transition from the ground to the $3p_\pm$ state.

Transi tion 1s (A$_1$) →	D$_n$ (Mg) complex:										
	D$_0$	D$_1$	D$_2$	D$_3$	D$_4$	D$_5$	D$_6$	D$_7$	D$_8$	D$_9$	D$_{10}$
2p$_0$	83.86				57.91	MP 54.59	MP 53.12	52.20	48.80	38.43	30.77
2p$_\pm$	MP 88.87	82.36	MP 80.61	MP 69.32	MP 62.98	59.56	58.10	57.06	53.94	MP 43.66	35.73
3p$_\pm$	MP 92.25	MP 85.65	83.86	72.60	66.23	62.93	61.39	60.32	57.22	MP 46.91	38.99
E_{Dn} (meV)	95.37		86.98	75.72	69.35	65.96	64.51	63.46	58.60	50.03	42.11

In relation to the observation of the multiplicity of shallow donors in excitation spectra of Si:Mg samples we note that these data are supported by Hall measurements on selected samples carried out immediately after doping and after a long storage time at room temperature, see next Section.

4. Discussion

Among the important results of the present study is the observation of a variety of shallow donors in Si:Mg samples obtained by doping high-purity Si, with small amounts of oxygen and carbon. We suggest that the multiplicity of centers is related to the formation of electrically active clusters of Mg atoms, similar to those observed for interstitial oxygen in Si. Mg clusters embedded in the Si lattice are formed due to the interaction of Mg atoms with each other and with atoms of the host lattice.

The variety of electron binding energies observed for Mg-related donors indicates on a number of configurations that Mg atoms can form in the silicon lattice. Such structures can both form different spatial configurations and include a different number of Mg atoms. The participation of other impurities – probably, oxygen and carbon – as well as defects in the silicon lattice can also be important for the electronic properties of a resulting cluster.

Following this model, one can expect that the final content of Mg-related shallow donors and their spatial distribution in a given sample may depend on details of doping and cooling regimes of a sample. This variety of scenarios may give rise to different ratios of concentrations of various centers in samples doped at similar conditions and even can be observed within the same wafer. Such a formation process is similar to that which is characteristic for the origin of thermal donors in Si. Thermal donors (TDs) are known to have a variety of ionization energies dependent on the configuration of the oxygen blocks in Si–O bonds of the cluster, see Ref. [2].

Following the discussed analogy, we point out the observation of "excess" Mg in Si:Mg samples, which do not show electrical activity. Such a phenomenon is similar to that observed in silicon containing oxygen-related thermal donors, where SiO_2 precipitation can be seen: such a process is known to accompany the formation of thermal donors [2].

We note that, due to the low concentrations of Mg-related shallow donors, some of them might be not observed in particular Si:Mg samples in our experiment: Only the most favorable bond structures may be formed at quantities allowing their observation in the IR absorption spectra of a given sample. Additional information that could be useful in increasing the understanding of the Mg-related shallow donors at such low concentrations could be delivered by photoluminescence (PL) investigations. Indeed, a number of no-phonon lines, not earlier observed in PL spectra of n-Si, was revealed in the low-temperature exciton luminescence spectra taken from a few Si:Mg samples in the frame of study of Mg isotopic fingerprints in ^{28}Si [15]. Determination of shallow Mg-related donors can be used for identification of localized centers linked to these exciton recombination transitions other than the

previously identified on isolated Mg and D (Mg,X≠Mg) pairs.

In general, oxygen-related TDs are referred to He-like, double donors, due to the appearance of absorption lines in IR spectra of compensated samples, which can be attributed to transitions associated with singly ionized deep centers, TDD0 to TTD9 [3,4]. We did not observe (possible) singly ionized states of D_n (Mg) and ED_n (Mg) centers in the specially boron-compensated n-Si:Mg:B samples (#MgB1,2,3), apparently due to relatively weak transition intensities caused by a low concentration of the centers. Thus, we cannot judge whether D_n (Mg) and ED_n (Mg) centers in the investigated samples are of H- or He-type. We notice in this respect that more shallow O-related TDs are considered as single H-like donor centers. These include those coupled to nitrogen or/and carbon (so called ultrashallow thermal donors in Si), which exhibit binding energies down to about 28 meV [10].

The analysis of the quadratic Zeeman effect for the D (Mg,X) donors in Si [25] shows that centers having a single outer/excess electron of atom X, either interstitial or substitutional, to form the bond to interstitial Mg, behave similarly to H-like donors. Transitions associated with these D (Mg,X) centers occur in the far-IR part of absorption spectra. On the other hand, pairing with another Mg or O atom (both are characterized by two, excess or missing, electrons in the outer shell) forms complexes with a spatial localization more similar to those of double donor centers, and transitions appear in the mid-IR range of spectra, in the vicinity of intracenter transitions of the Mg^0 isolated donor. Applying this observation to the centers reported in the present study, one may argue that D_n (Mg) centers tend to act as centers with a single weakly bound electron, while evolving ED_n (Mg) centers are more similar to double donor centers.

Interstitial oxygen, unavoidable in Si, is one of most aggressive traps for mobile interstitial isolated Mg. This effect was first found in oxygen-rich Si:Mg [30] and later in low-oxygen Si:Mg [12] as well as in this work by direct observation of the increasing intensity of D (Mg,O) transitions in their IR absorption spectra. Apparently, multi-atom complexes with participation of oxygen, D (nMg,O), are the final destination of Mg in complexes assigned in this work to evolved ED_n (Mg) centers.

The long-time storage of Si:Mg samples at room temperature is known to be accompanied by a decrease in concentration of the interstitial Mg [12]. The Hall effect data obtained on our samples in the course of their storage show that a decay in density of free electrons observed in a sample (which proceeds through diminishing the concentration of deep Mg donors) is partly compensated by generation of new shallow donors. Such a scenario of dynamics of electronic states in a crystal may be interpreted as a process where isolated highly mobile Mg interstitials are consumed by electrically active clusters of Mg atoms with low ionization energies that are formed and grow in the volume.

Data of this work refer to samples prepared mainly by a standard technological procedure. More detailed information on the nature of these new shallow donors can be obtained through studying results of post-diffusion annealing of samples – similar to the approach used to investigate thermal donors in Si [3].

5. Summary

To summarize, a multiplicity of shallow Mg-related complexes with energy spectra similar to those of well-known hydrogen-like impurities as well as of double donors in Si has been found. These new donors are observed in low temperature IR absorption spectra of Si doped with Mg by the high-temperature diffusion followed by slow or rapid cooling. The absorption lines of these centers are dense and fall into two distinct IR ranges: one below the neutral Mg center, from 30 to 95 meV, and the other one above, from 105 to 130 meV. It has been observed that the specific formation time of these two groups of centers can be divided into two times scales: some centers are immediately created in the course of diffusion/cooling, while the density of others increases at room temperature on the scale of years.

The difference in the sets of Mg-related shallow donors observed in

Table 4
Strongest intracenter transitions (in meV) of different ED_n (Mg) complexes in Si: Mg formed on a long-time scale (months-years). The uncertainty in the transition energies derived from the spectra is ±0.01 meV. The binding energy is determined by adding 3.12 meV to the energy of transition from the ground to the assigned $3p_\pm$ state.

Transition	Evolving ED_n (Mg) complex:			
1s (A$_1$) → 2p$_0$	ED_0	ED_1	ED_2	ED_3
$2p_\pm$	126.52	124.44	112.71	MP
			112.87	110.68
			112.99	110.73
$3p_\pm$	129.68	127.71	116.16	113.97
E_{ED_n} (meV)	132.8	130.8	119.3	117.1

samples doped at similar conditions suggests possible different kinetic processes of decomposition of a solid solution of Mg in a Si crystal, right after the high-temperature stage of diffusion, that results in the formation of electrically active Mg-related complexes. We note that such a phenomenon may give an inhomogeneous distribution of shallow donors within a Si:Mg crystal.

The experimental data of the present study suggest that there exists an analogy of these shallow centers to so called thermal donors in silicon, which are extensively studied and related to the presence of oxygen in Si crystals.

Author statement

Concept: S. G. Pavlov, Yu. A. Astrov, L. M. Portsel, N. V. Abrosimov.

Material Processing: Yu. A. Astrov, L. M. Portsel, V. B. Shuman, A. N. Lodygin, N. V. Abrosimov.

Analytical spectroscopy: Yu. A. Astrov, L. M. Portsel, V. B. Shuman, A. N. Lodygin, N. V. Abrosimov.

Infrared Spectroscopy: S. G. Pavlov, H.-W. Hübers.

Data Analysis: S. G. Pavlov, Yu. A. Astrov, L. M. Portsel.

Writing – original draft: S. G. Pavlov, Yu. A. Astrov.

Writing – review & editing: Yu. A. Astrov, L. M. Portsel, V. B. Shuman, A. N. Lodygin, N. V. Abrosimov, H.-W. Hübers.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

References

[1] R.W. Jansen, O.F. Sankey, Phys. Rev. B 33 (1986) 3994–4001, https://doi.org/10.1103/PhysRevB.33.3994.

[2] P. Wagner, C. Holm, E. Sirtl, R. Oeder, W. Zulehner, in: P. Grosse (Ed.), Advances in Solid State Physics, vol. 24, Springer, Berlin, Heidelberg, 1984, pp. 191–228, https://doi.org/10.1007/BFb0107451.

[3] P. Wagner, J. Hage, Appl. Phys. A 49 (1989) 123–138, https://doi.org/10.1007/BF00616290.

[4] J. Michel, L.C. Kimerling, Semiconduct. Semimet. 42 (1994) 251–287, https://doi.org/10.1016/S0080-8784(08)60250-1.

[5] T.E. Gilmer Jr., R.K. Franks, R.J. Bell, J. Phys. Chem. Solid. 26 (1965) 1195–1204, https://doi.org/10.1016/0022-3697(65)90098-3.

[6] M. Suezawa, K. Sumino, H. Harada, T. Abe, Jpn. J. Appl. Phys. 25 (1986) L859, https://doi.org/10.1143/JJAP.25.L859.

[7] Zhiyi Yu, Y.X. Huang, S.C. Shen, Appl. Phys. Lett. 55 (1989) 2084, https://doi.org/10.1063/1.102090.

[8] J. Hartung, J. Weber, Phys. Rev. B 48 (1993) 14161, https://doi.org/10.1103/PhysRevB.48.14161.

[9] R.E. Pritchard, M.J. Ashwin, J.H. Tucker, R.C. Newman, E.C. Lightowlers, T. Gregorkiewicz, I.S. Zevenbergen, C.A.J. Ammerlaan, R. Falster, M.J. Binns, Semicond. Sci. Technol. 12 (1997) 1404, https://doi.org/10.1088/0268-1242/12/11/012.

[10] A. Hara, Jpn. J. Appl. Phys. 34 (1995) 3418, https://doi.org/10.1143/JJAP.34.3418.

[11] V.N. Shastin, R.Kh. Zhukavin, K.A. Kovalevsky, V.V. Tsyplenkov, V.V. Rumyantsev, D.V. Shengurov, S.G. Pavlov, V.B. Shuman, L.M. Portsel, A.N. Lodygin, Yu. A. Astrov, N.V. Abrosimov, J.M. Klopf, H.-W. Hübers, Semiconductors 53 (2019) 1234, https://doi.org/10.1134/S1063782619090197.

[12] Yu.A. Astrov, V.B. Shuman, L.M. Portsel, A.N. Lodygin, S.G. Pavlov, N. V. Abrosimov, V.N. Shastin, H.-W. Hübers, Phys. Status Solidi 214 (2017) 1700192, https://doi.org/10.1002/pssa.201700192.

[13] (a) V.B. Shuman, A.A. Lavrent'ev, Yu A. Astrov, A.N. Lodygin, L.M. Portsel, Semiconductors 51 (2017) 1, https://doi.org/10.1134/S1063782617010237; (b) V.B. Shuman, Yu A. Astrov, A.N. Lodygin, L.M. Portsel, Semiconductors (2017) 1031, https://doi.org/10.1134/S1063782617080292.

[14] R.J.S. Abraham, A. DeAbreu, K.J. Morse, V.B. Shuman, L.M. Portsel, A.N. Lodygin, Yu.A. Astrov, N.V. Abrosimov, S.G. Pavlov, H.-W. Hübers, S. Simmons, M.L. W. Thewalt, Phys. Rev. B 98 (2018), 045202, https://doi.org/10.1103/PhysRevB.98.045202.

[15] R.J.S. Abraham, A. DeAbreu, K.J. Morse, V.B. Shuman, L.M. Portsel, A.N. Lodygin, Yu.A. Astrov, N.V. Abrosimov, S.G. Pavlov, H.-W. Hübers, S. Simmons, M.L. W. Thewalt, Phys. Rev. B 98 (2018) 205203, https://doi.org/10.1103/PhysRevB.98.205203.

[16] R.J.S. Abraham, V.B. Shuman, L.M. Portsel, A.N. Lodygin, Yu.A. Astrov, N. V. Abrosimov, S.G. Pavlov, H.-W. Hübers, S. Simmons, M.L.W. Thewalt, Phys. Rev. B 99 (2019) 195207, https://doi.org/10.1103/PhysRevB.99.195207.

[17] A.L. Thilderkvist, M. Kleverman, H.G. Grimmeiss, Phys. Rev. B 49 (1994) 16338–16348, https://doi.org/10.1103/PhysRevB.49.16338.

[18] L.T. Ho, Phys. Status Solidi 210 (1998) 313–316, https://doi.org/10.1002/pssc.200306203.

[19] N.V. Abrosimov, D.G. Aref'ev, P. Becker, H. Bettin, A.D. Bulanov, M.F. Churbanov, S.V. Filimonov, V.A. Gavva, O.N. Godisov, A.V. Gusev, T.V. Kotereva, D. Nietzold, M. Peters, A.M. Potapov, H.-J. Pohl, A. Pramann, H. Riemann, P.-T. Scheel, R. Stosch, S. Wundrack, S. Zakel, Metrologia 54 (2017) 599, https://doi.org/10.1088/1681-7575/aa7a62.

[20] L.M. Portsel, V.B. Shuman, A.A. Lavrent'ev, A.N. Lodygin, N.V. Abrosimov, Yu. A. Astrov, Semiconductors 54 (2020) 393, https://doi.org/10.1134/S1063782620040120.

[21] S.G. Pavlov, N. Deßmann, A. Pohl, V.B. Shuman, L.M. Portsel, A.N. Lodygin, Yu. A. Astrov, S. Winnerl, H. Schneider, N. Stavrias, A.F.G. van der Meer, V. V. Tsyplenkov, K.A. Kovalesky, R.Kh. Zhukavin, V.N. Shastin, N.V. Abrosimov, H.-W. Hübers, Phys. Rev. B 94 (2016), 075208, https://doi.org/10.1103/PhysRevB.94.075208.

[22] K. Matsumoto, Y. Uenaka, Y. Seto, H. Yashiro, H. Nakamura, T. Kimura, T. Uchino, Synthetic condition to generate magnesium-related acceptor levels in silicon, J. Appl. Phys. 108 (2010) 113706, https://doi.org/10.1063/1.3517412.

[23] H. Ch Alt, Y. Gomeniuk, B. Wiedemann, H. Riemann, J. Electrochem. Soc. 150 (2003) G498, https://doi.org/10.1149/1.1589023.

[24] G. Kissinger, Oxygen precipitation in silicon, in: Y. Yoshida, G. Langouche (Eds.), Defects and Impurities in Silicon Materials, Lecture Notes in Physics, vol. 916, Springer, Tokyo, 2015, https://doi.org/10.1007/978-4-431-55800-2_6.

[25] S.G. Pavlov, D.L. Kamenskyi, Yu.A. Astrov, V.B. Shuman, L.M. Portsel, A. N. Lodygin, N.V. Abrosimov, H. Engelkamp, A. Marchese, H.-W. Hübers, Phys. Rev. B 102 (2020) 115205, https://doi.org/10.1103/PhysRevB.102.115205.

[26] B. Pajot, Optical Absorption of Impurities and Defects in Semiconducting Crystals: I. Hydrogen-like Centres, Springer, Berlin, 2010, https://doi.org/10.1007/b135694.

[27] R.A. Faulkner, Phys. Rev. 184 (1969) 713, https://doi.org/10.1103/PhysRev.184.713.

[28] L.T. Ho, Proc. The Joint 30th Int. Conf. on Infrared and Millimeter Waves and 13th Int. Conf. on Terahertz Electronics, 19.-23. Sept. 2005, vol. 1, Williamsburg, Virginia, USA, 2005, pp. 170–171, https://doi.org/10.1109/ICIMW.2005.1572462.

[29] E. Janzen, R. Stedman, G. Grossmann, H.G. Grimmeiss, Phys. Rev. B 29 (1984) 1907–1918, https://doi.org/10.1103/PhysRevB.29.1907.

[30] L.T. Ho, Physica B 302–303 (2001) 197–200, https://doi.org/10.1016/S0921-4526(01)00428-8.