Isotope effect on the lifetime of the $2p_0$ state in phosphorus-doped silicon


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The low-temperature (∼5 K) phonon-assisted relaxation of the $2p_0$ state of phosphorus donors in isotopically pure, monocrystalline $^{28}$Si has been studied in the time domain using a pump-probe technique. The lifetime of the $2p_0$ state in $^{28}$Si:P is found to be 235 ps, which is 16% larger than the lifetime of a reference Si:P sample with a natural isotopic composition. The interaction of the $2p_0$ state with intervalley $g$-type longitudinal acoustic and $f$-type transverse acoustic phonons determines its lifetime. This interaction, which depends on the homogeneity of the crystal, becomes weaker in $^{28}$Si because of its more perfect crystal lattice compared to natural Si, and this leads to a longer lifetime. The difference between the linewidths of the $1s(A_1) → 2p_0$ transition in $^{28}$Si:P and natural Si:P is more than a factor of two. It follows that linewidth broadening due to isotopic composition is an inhomogeneous process.

I. INTRODUCTION

Silicon (Si) is the most widely used and the most important semiconductor. Despite many experimental and theoretical investigations, the lifetimes of excited states in $n$- and $p$-type-doped Si remain a puzzle. These lifetimes have been determined for a number of dopants and excited states either by direct time-domain measurements or from the linewidths of transitions in absorption spectra. However, theoretical understanding is still lacking. For example, the lifetime of the $2p_0$ state in Si doped by phosphorus (Si:P) has been measured as 205 ps (Ref. 1), while models predict lifetimes of 40 ps or 1.1 ns. This indicates that the interaction of the donor electron with the host lattice is not fully understood.

In addition, several exciting applications rely on transitions between states of group V donors in Si. These include using shallow donors embedded in a Si matrix as active elements in qubits for quantum computing and spintronics, terahertz lasers operating on donor optical transitions, and terahertz Raman lasers. All of these applications require a detailed understanding of the lifetimes of excited states.

So far, most investigations have been done on Si crystals with natural isotopic composition ($^{28}$Si). In this paper, we focus on high-quality, isotopically enriched $^{28}$Si:P crystals. These crystals are an excellent material for fundamental investigations, since their structure is almost perfect. Because of their perfection, such $^{28}$Si crystals are a promising candidate for the new definition of the kilogram. Although the composition of natural Si (92.23% $^{28}$Si, 4.67% $^{29}$Si, and 3.1% $^{30}$Si) is close to that of monoisotopic $^{28}$Si, the isotopic composition can significantly influence the material properties. Some examples are the thermal conductivity, which increases by a factor of eight in $^{28}$Si (Ref. 14); the heat capacity, which increases with isotopic mass; the lattice parameter, which decreases with isotopic mass; the band gaps of Si (Ref. 17); the energy structure and optical transitions of impurity centers in Si (Ref. 3); and the phononic spectra.

In this paper, we report on direct lifetime measurements of the $2p_0$ state in phosphorus-doped, isotopically enriched $^{28}$Si using a terahertz pump-probe technique on the $1s(A_1) → 2p_0$ transition. We carried out the same measurements with phosphorus-doped $^{29}$Si. By comparing the results, we are able to study the influence of isotopic composition on the lifetime of the $2p_0$ state.

II. ENERGY LEVELS OF GROUP V DONORS IN SILICON

The energy levels of group V donors in Si are special, because the sixfold degeneracy of donor states is partially lifted because of valley-orbit interaction. Effective mass theory (EMT) is not sufficient to describe the donor binding energy correctly, because the wave functions of the symmetric $s$-type states have significant amplitudes close to the donor ion, where the coulomb potential is less screened. This causes splitting (also called chemical splitting), and a downshift in energy of the $s$ levels, which is most pronounced for the $1s$ ground state (Fig. 1(a)). The $1s$ state splits into $1s(A_1)$ singlet, $1s(T_2)$ triplet, and $1s(E)$ doublet states, with the $1s(E)$ and $1s(T_2)$ states close to what is predicted by EMT and the $1s(A_1)$ ground state significantly lower. The decay of an electron is controlled by phonon-assisted relaxation and at a low temperature strongly depends on the energy gap to the nearest lower state. The relatively large energy gaps between the lowest excited
Theoretical estimates show that the indirect path via the split-
ning at 18 meV is the process that dominates the decay from the
second decay into the ground state [Fig. 1(b)]. From the
interaction. Through this approach, the specific features of the
donor states affect the decay times of these states such that they
are relatively long lived. For Si:P, the lowest p-type state, 2p₀,
has the largest energy gap to the lower 1s(E) and 1s(T₂) donor
states and therefore the longest lifetime in comparison with
other odd parity states. This effect makes Si doped by group
V donors, and in particular the 2p₀ state in Si:P, attractive for
terahertz lasers and optical manipulation of impurity states.
When considering the lifetime of the 2p₀ state and the decay of
electrons into the 1s(A₁) state, one has to consider the inter-
mediate states 1s(E) and 1s(T₂). In the case of Si:P electrons,
which are captured in the 2p₀ state, there are essentially two
ways to reach the 1s(A₁) ground state: the electrons either
decay directly into the 1s(A₁) state or undergo a two-step
process—a first decay into one of the split-off 1s states,
followed by a second decay into the ground state [Fig. 1(a)].
Theoretical estimates show that the indirect path via the split-
off states is the dominant process. Electrons first decay into
the 1s(E) and 1s(T₂) states by emission of intervalley g-type
longitudinal acoustic (g-LA) and f-type transverse acoustic
(f-TA) phonons. By emission of g-TA phonons, they further
decay into the 1s(A₁) ground state. The latter step is a much
faster process,²¹ because the g-TA phonon is in resonance with
the 1s(E),1s(T₂) → 1s(A₁) transitions [Fig. 1(b)]. From the
symmetry of the donor states, it follows that intravalley scatter-
ing from the 1s(T₂) state into the ground state is not allowed.²²

In principle, the lifetime of a state can be indirectly inferred
from the absorption linewidth of an impurity transition involv-
ing this state—provided that the line is predominantly lifetime
(homogeneously) broadened. In practice, this is challenging,
because the measured absorption linewidth is a convolution of
the natural, homogeneous linewidth; the instrument response;
and various inhomogeneous broadening effects. The most
important ones are Stark broadening from random electric
fields, concentration broadening due to overlap of excited state
wave functions, and strain broadening. They are caused by
impurities and lattice defects. Recently isotopic broadening
has been identified as another inhomogeneous broadening
mechanism.²³ Because of its larger extent, the excited state
donor wave function samples a larger region of the crystal than
does the more confined ground state and thus always samples
distribution of isotopes close to the average. In contrast,
the confined ground state sees a greater fluctuation in the
distribution of isotopes. As a result, the energy of the excited
state is largely independent of the position of the donor; the
energy of the ground state fluctuates more strongly with donor
position. High-resolution Fourier transform infrared (FTIR)
absorption spectroscopy of the 1s(A₁) → 2p₀ transition
performed at a temperature of 1.5 K has revealed a linewidth
of 0.033 cm⁻¹ in isotopically enriched ²⁸Si with a phosphorus
concentration of N_p = 2 × 10¹⁵ cm⁻³, while the linewidth of
the same transition in natSi was found to be 0.082 cm⁻¹.²⁻³ If
it is assumed that the transition is homogeneously broadened,
then this corresponds to a lifetime of the 2p₀ state of 161 ps
for ²⁸Si and 65 ps for natSi. Time-domain pump-probe methods
yield the lifetime of a particular state provided that pump and
probe pulses are short with respect to the measured lifetime.
For example, the lifetime of the 2p₀ state in phosphorus-doped
natSi (N_p = 2 × 10¹⁵ cm⁻³) was measured by this method to
be 205 ± 18 ps at ~5 K.¹ Taking into account the different
types of samples, we are at liberty to assume a lifetime of
~160 to 200 ps for the 2p₀ state in Si. This assumes that the
transition is only homogeneously broadened. We show later
that this is not the case.

One of the disputed issues is the effect of isotope broadening
on the linewidth of intracenter optical transitions between
energy levels and the lifetime of the states of shallow donors
in Si. Recent theoretical calculations of the lifetime of the 2p₀
state in Si (Refs. 4 and 5) differ significantly from what has
been measured. Tsyplenkov et al. calculated the transition rate
for nonradiative transitions from the 2p₀ state to the 1s(E)
and 1s(T₂) states.⁴ The model is semiempirical, because it
constructs the envelop forms of the wave functions of the 1s
states on the basis of experimental data on the energy of the
eigenstate and uses the experimental data on electron-phonon
interaction. Through this approach, the specific features of the
short-range central cell potential of the donor are taken into
account. They calculated the decay rates of the 2p₀ → 1s(E),
1s(T₂) transitions, and it was shown that the lifetime of the 2p₀
state is ~40 ps.⁴ In contrast, Tsyterev et al. found the lifetime
for the same donor state to be ~1.1 ns.⁵ Their work is based
on ab initio computation of the electron-phonon interaction in
the framework of a density-functional perturbation approach
applied to an ideal crystal. It combines the matrix elements
of the electron-phonon coupling with the envelope function
approximation for the impurity wave functions.

III. EXPERIMENTAL PROCEDURE

Dislocation-free Si crystals with natural isotopic compo-
sition and isotopically pure ²⁸Si were grown in the [100]
direction by the float zone technique in an Ar atmosphere. The

FIG. 1. (Color online) (a) Energy levels of Si:P (Ref. 19). The
bold upward arrow indicates the pump transition. The downward
arrows indicate the possible decay paths. The green and red straight
arrows mark the path with the largest rate, while the dashed blue
arrow indicates the direct decay into the ground state. (b) Phonon
density of states (DOS) (Ref. 20). The lines indicate the positions of
the transitions shown in (a). The interaction with the g-LA and f-TA
phonons at 18 meV is the process that dominates the decay from the
2p₀ state. The g-TA phonon is in resonance with the 1s(E), 1s(T₂) → 1s(A₁) transitions.
starting material for the $^{28}$Si crystal growth was produced in the framework of the Avogadro project.\textsuperscript{24} The content of the $^{28}$Si isotope in the crystal exceeds 0.99994; the oxygen and carbon concentrations measured by infrared spectroscopy are $\sim 4 \times 10^{14}$ and $\sim 2 \times 10^{14}$ cm$^{-3}$, respectively. The crystals were phosphorus-doped using gaseous phosphine. The doping concentrations of the Si crystals we use are $2 \times 10^{15}$ cm$^{-3}$ ($^{28}$Si) and $4 \times 10^{15}$ cm$^{-3}$ ($^{nat}$Si). Both samples were cut into rectangular parallelepipeds with an area of $7 \times 7 \text{mm}^2$ and a thickness of 0.39 mm ($^{28}$Si) and 0.2 mm ($^{nat}$Si) and were chemically and mechanically polished with a wedge angle of $1^\circ$ in order to avoid the effect of standing waves in the sample.

For the time-domain pump-probe measurements, we used the free electron laser for infrared experiments (FELIX) at the Foundation for Fundamental Research on Matter (FOM) in the Netherlands. FELIX emits macropulses of $\sim 6 \mu$s with a repetition frequency of 10 Hz. Each macropulse consists of a train of micropulses with a duration of $\sim 10$ ps, separated by 40 ns. The experimental arrangement is a three-beam, balanced pump-probe technique described in Ref.\textsuperscript{25} (Fig. 2). From the total power of the initial pulse, 5\% is split off by a beam splitter. A second beam splitter separates this weak pulse into a probe beam and a reference beam. The relative delay between the strong pump and the weak probe beam can be varied between 0 and 1 ns. The reference beam is delayed by 20 ns with respect to the probe beam and measures the transmission of the unexcited sample. The three beams are focused onto the sample, and the transmitted probe and reference pulses are detected with a Ge:Ga photodetector. Its bias voltage is modulated at 25 MHz, which results in signals with the opposite sign for the probe and the reference beam. When no pump pulse is applied, the system is balanced; i.e., the integrating electronics shows a zero output signal.

The experiments were performed on the 1$s(A_1) \rightarrow 2p_0$ transition. The measured relaxation rate of the $2p_0$ state includes contributions from the relaxation rates of the 1$s(E)$ and 1$s(T_2)$ states. However, this effect is small and can be neglected because of the fast relaxation from these states ($\sim 10^{11}$ s$^{-1}$).\textsuperscript{5,10} The peak pump power on the sample at the $1s(A_1) \rightarrow 2p_0$ transition energy (34.1 meV) was estimated from the measured average output pulse energy to be $\sim 60$ nJ per micropulse. The pump power was attenuated up to 35 dB by a set of wire-grid attenuators.

The samples were strain-free mounted on a copper holder, which in turn was mounted to the cold finger of a liquid helium flow cryostat. The temperature of the sample was $\sim 5$ K. At this temperature, all donor-related electrons are in the 1$s(A_1)$ ground state. When excited by the pump beam, electrons populate the state with an energy separation from the ground state equal to the pump photon energy. This nonequilibrium electron population relaxes into the ground state with a characteristic time $T_1$. The change in transmission of the probe beam, which passes the Si sample, reflects changes in the optically induced nonequilibrium population of the excited state. By varying the time delay between pump and probe beams and measuring the transmittance through the sample as a function of this delay, we can determine $T_1$.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

The time-dependent transmittance of the probe beam was analyzed by a similar procedure to that described in Ref. 1. Prior to fitting, a constant offset was subtracted from the measured data. The offset is caused by nonperfect balancing, which is difficult to avoid even under ideal circumstances. We verified that it is an experimental artifact and not caused by an intracenter relaxation process by measuring the transmission signal when the FELIX wavelength is tuned to be out of resonance with any intracenter transition. We found that the offset is present in this situation as well. The data were fitted with a single exponential $C_0 \times \exp(t/T_1)$. As a control experiment, we determined the $T_1$ time of the $2p_0$ state in a $^{nat}$Si:P reference sample. The result is $T_1 = 203 \pm 15$ ps, which is in excellent agreement with the lifetime of $T_1 = 205 \pm 18$ ps published by Vinh et al.\textsuperscript{1}

Examples of the change of the transmittance for the $^{28}$Si crystal as a function of delay between pump and probe pulses are shown in Fig. 3 for different micropulse energies. For all pump powers, the decay is well described by a single exponential with the decay parameter $1/T_1$. In Fig. 4, the

FIG. 2. (Color online) Scheme of the experimental setup.

FIG. 3. (Color online) Transmittance of $^{28}$Si induced by the pump beam as a function of delay between pump and probe pulse for different micropulse energies (given by the numbers in the figure). The micropulse length is 10 ps.
values of $T_1$ are shown as a function of micropulse energy. They are independent of the pump energy and the mean value is $T_1 = 235 \pm 15$ ps. This value is 16% larger than the value of $203 \pm 15$ ps measured for $^{29}$Si:P. It is instructive to compare these time-domain results with those extracted from the linewidth measurements of the $1s(A_1) \rightarrow 2p_0$ transition measured by FTIR spectroscopy. The linewidth in $^{28}$Si is found to be 0.033 cm$^{-1}$, while for $^{29}$Si it is almost 2.5 times larger and amounts to 0.082 cm$^{-1}$. In comparison, the pump-probe measured lifetimes are different by only $\sim 16\%$. This shows that broadening caused by isotopic composition is predominantly an inhomogeneous process that affects the linewidth but not the lifetime.

Since the lifetime of the $2p_0$ state is determined by the emission of phonons, the different lifetimes of the $2p_0$ state in $^{28}$Si and $^{29}$Si indicate that the electron-phonon interaction in both materials is different. One factor that affects the electron-phonon interaction is the nature of the intervalley scattering by $g$-LA and $f$-TA phonons, which determines the relaxation process of the $2p_0$ state. In contrast, $g$-TA phonons determine the decay of the $1s(E)$ and $1s(T_2)$ states. In an ideal Si crystal, the deformation potential is zero for electron intervalley transitions along high-symmetry directions in the Brillouin zone. The presence of isotopes lowers the symmetry of the crystal, allowing transitions with the emission of $g$-LA and $f$-TA phonons, in momentum directions that are otherwise forbidden. Thus, the deformation potential changes in $^{29}$Si. This is emphasized by the peculiarities of the $2p_0$ state, which can be represented by an $A_1$, an $E$, and a $T_2$ component—similar to the $1s$ ground state, although the components of the $2p_0$ state are spectrally not resolved. In case of a perfect Si crystal, electrons from the ground state can be directly photoexcited only into the $A_1$ and $E$ components of the $2p_0$ state. However, scattering due to crystal imperfections such as different isotopes enables the transfer of electrons into the $T_2$ component. This opens an additional channel for relaxation and reduces the lifetime of the $2p_0$ state in $^{29}$Si compared to $^{28}$Si. In a microscopic picture, one may consider the unit cells in $^{28}$Si. These are all equal, and the displacement of neighboring unit cells caused by acoustic phonons is the same; i.e., there is no relative displacement of unit cells. In $^{29}$Si, there is a significant probability that neighboring unit cells have different mass. Scattering by $g$-LA and $g$-TA phonons leads to a relative displacement of unit cells with different mass, which in turn leads to additional strain, an increased deformation potential, and a reduced lifetime of the $2p_0$ state.

In the virtual-crystal approximation, the phonon frequencies of a monoatomic crystal are proportional to $\langle M \rangle^{-1/2}$, where $\langle M \rangle$ is the average mass of the isotopes in the crystal weighted by the corresponding isotopic abundance. Therefore, phonon frequencies of $^{29}$Si are expected to be larger than those of $^{28}$Si, and the phonon density of states is expected to shift toward higher frequencies. A manifestation of this effect is the shift of the peak in the Raman spectrum from 524 cm$^{-1}$ for $^{28}$Si to 525 cm$^{-1}$ for $^{29}$Si:P, which was also found for the Si samples of this paper. This also might affect the transitions involved in the decay of the $2p_0$ state. However, the shift is small; therefore, this contribution to the decrease of the lifetime in $^{29}$Si is expected to be negligible.

It is instructive to compare the results for $n$-type Si with those obtained for $p$-Si for which the effect of isotopic randomness has been studied experimentally and theoretically. It was found that the random distribution of the isotopes around the acceptor leads to a ground-state splitting and the shift of the center of mass of the transition energies causes a broadening. For Al, the broadening is $\sim 0.3$ cm$^{-1}$, which is $\sim 2\%$ of the transition energy from the ground state to the next-higher excited state ($1\Gamma_1^g$). This indicates that the effect of isotopic randomness on the lifetime of a state is the qualitatively the same in $p$-type and $n$-type Si, although it differs quantitatively.

V. CONCLUSIONS

We have measured the lifetimes of the $2p_0$ state in $^{28}$Si and $^{29}$Si using a terahertz pump-probe technique. The lifetime of $^{28}$Si is found to be 16% larger than that of $^{29}$Si. This is a much smaller difference than that found for the absorption linewidths of the $1s(A_1) \rightarrow 2p_0$ transition in low-doped Si crystals. From the time-domain measurements, it follows that linewidth broadening due to isotopic composition is an inhomogeneous process. The longer lifetime found for $^{28}$Si compared to $^{29}$Si can be attributed to the higher symmetry of the $^{28}$Si crystal and a less pronounced interaction of the $^{28}$Si ground state with the $2p_0$ state, as well as the $1s(E)$ and $1s(T_2)$ states with the $g$-LA and $f$-TA phonons, which determine its lifetime. As a result, the lifetime of the $2p_0$ state in $^{29}$Si is shorter. Our results are in excellent agreement with previous lifetime measurements on $^{29}$Si. However, there is a large discrepancy to theoretical calculations. In order to gain a quantitative understanding of the basic processes that govern the relaxation processes in impurity centers in semiconductors, it is desirable that the theoretical models are further improved. For this purpose, the well-investigated system Si:P represents an excellent model case.

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