Direct observation of the donor nuclear spin in a near-gap bound exciton transition: ^{31}P in highly enriched ^{28}Si*

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We report on ultrahigh resolution studies of the bound exciton states associated with the shallow acceptor B and the shallow donor P in highly enriched ^{28}Si using a tuneable single frequency laser to perform photoluminescence excitation spectroscopy. The linewidths and fine structure of the transitions, which were too narrow to be resolved previously using an available photoluminescence apparatus, are now fully revealed. The P bound exciton transition shows a complicated additional structure, which the Zeeman spectroscopy demonstrates to be a result of the splitting of the donor ground state by the hyperfine interaction between the spin of the donor electron and that of the ^{31}P nucleus. The ^{31}P nuclear spin populations can thus be determined, and hopefully modified, by optical means. The predominant Auger recombination channel of these bound excitons is used to observe the same resolved hyperfine transitions in the photocurrent spectrum. This demonstrates that donors in specific electronic and nuclear spin configurations can be selectively photoionized. Possible applications of these results to quantum computing and quantum information systems are discussed. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2723181]

I. INTRODUCTION

Virtually all semiconductors consist of mixtures of stable isotopes, and the recent ability to modify the isotopic composition, and to study how these changes affect the physical properties of a given semiconductor, has led to a wide range of developments.[1–3] An earlier study of the photoluminescence (PL) of shallow bound excitons (BE) in enriched ^{28}Si revealed not only the expected[3] changes of band gap energy and wavevector conserving phonon (WCP) energies with the change in average isotopic mass, but also the quite unexpected result that the linewidths of the no-phonon (NP) transitions of the P and B BEs in ^{28}Si were much narrower than ever seen before in the most perfect Si of natural isotopic composition.[4] In fact, the observed linewidths in ^{28}Si were essentially at the instrumental resolution limit of 1.7 μeV (the best resolution for Si PL spectroscopy using commercially available instrumentation), and as a result it was only possible to set an upper limit of ~620 neV on the actual linewidths in ^{28}Si.[4] Here we report a different spectroscopic approach which allows the BE NP transitions to be fully resolved in an improved sample of ^{28}Si, resulting in transitions with a full width at half maximum (FWHM) as small as 150 neV. The P donor BE shows a well-resolved structure due to the hyperfine splitting of the donor ground state resulting from the coupling between the spin 1/2 electron and the spin 1/2 nuclear spin of ^{31}P, as measured previously[5]

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using neutral donor (D^0) electron spin resonance (ESR) spectroscopy. The P BE hyperfine structure can also be resolved in the photocurrent spectrum, detecting the free electrons released by the Auger recombination of the resonantly created BEs. A number of potential applications of these results to quantum computing and quantum information systems are discussed.

II. EXPERIMENT

It should be emphasized that even in natural Si (92.23% ^{28}Si, 4.67% ^{29}Si, 3.10% ^{30}Si), the 5 μeV FWHM of the phosphorus BE no-phonon luminescence transition was among the narrowest near-gap transitions known in semiconductors.[4] The discovery that it narrowed to the instrumental resolution limit in highly enriched ^{28}Si was the earliest indication of the importance of inhomogeneous isotope broadening in determining the observed linewidth of this and other electronic transitions in Si.[4,6] The resolution limit imposed by the use of commercial spectrometers, together with the weak luminescence signal characteristic of BE in Si, has been overcome by studying the NP transitions of the BEs in absorption rather than in emission, using a tunable single-frequency laser source with a linewidth of less than 0.3 neV, and detecting the weak absorption by the resulting luminescence signal (photoluminescence excitation spectroscopy, or PLE), using the transverse optical (TO) WCP replica, which is well separated in energy from the NP transitions ($\sim$58 meV lower in energy). An improved sample of ^{28}Si, here labeled ^{28}Si$-a$, was used in the present study, with an isotopic enrichment of 99.991%, and a much higher chemical purity, having phosphorus $\sim 2\times 10^{12}$ cm^{-3} and boron $\sim 5\times 10^{13}$ cm^{-3}, as measured by photoluminescence, and carbon $<5\times 10^{14}$ cm^{-3} (detection limit) as measured by local vibrational mode absorption. Two other samples enriched to 99.983% (^{28}Si$-b$) and 99.92% (^{28}Si$-c$) were also studied.

The distributed feedback Yb-doped single-frequency fiber laser (Koheras A/S) could be temperature tuned over the region of interest, and the laser frequency was monitored to one part in 10^7 with a wavemeter (Exfo/Burleigh). The laser output was amplified to 500 mW in an Yb-doped fiber amplifier (Keopsys), mechanically chopped to allow for lock-in detection of the signal, and focused onto the edge of the sample. Samples were loosely mounted (to avoid strain) in a reflecting cavity to optimize the weak luminescence signals, and immersed in liquid He. Additional above-gap excitation to photoneutralize the impurities (note that the ^{28}Si$-a$ and b samples were p-type) was provided by a 1184 meV (1047 nm) Nd:YLF laser at power levels between 1 and 500 mW. While these optical power levels appear high, both laser beams are only weakly absorbed in the sample, and sample heating is expected to be minimal. The luminescence signal was separated from the intense scattered excitation radiation using a 3/4 m double monochromator and detected with a Ge photoconductive detector (North Coast) operated at 77 K. The resolution of the double monochromator was far less than what would be required to separate the BE components studied here, so that the PLE detection was completely non-selective. The pump/luminescence beams entered/exited the sample perpendicular to the magnetic field direction, but due to the high transparency and refractive index of Si, and the high collection efficiency geometry employed here, multiple reflections would tend to reduce any direction and polarization effects.

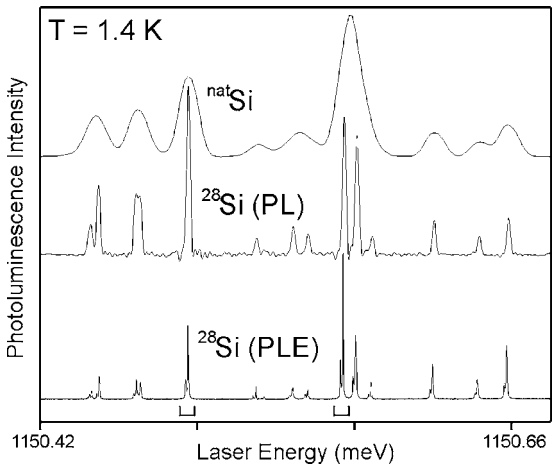

FIG. 1. The new PLE spectrum of the B BE in sample ^{28}Si$-a$ (bottom) is compared with the best previous (Ref. 4) PL spectra of ^{28}Si and ^{nat}Si. The ^{nat}Si spectrum has been shifted down in energy by 0.114 meV to compensate for the shift of the band gap with isotopic composition.

III. RESULTS

We begin by briefly discussing the results for the B acceptor BE, which will be described in more detail elsewhere. In Fig. 1 we compare the new PLE spectrum of the B BE NP transitions in the ^{28}Si$-a$ sample with the best previous[4] PL spectra in ^{28}Si and ^{nat}Si. The nine components resolved in the PL spectrum of ^{nat}Si are further resolved into 14 components in the PL spectrum of ^{28}Si, and 32 components in the PLE spectrum of ^{28}Si, which in addition to being fully resolved also has a much higher signal-to-noise ratio than the PL spectrum. Each component in the B BE PLE spectrum occurs as an identical doublet with a splitting of 1.34 μeV and a 20/80 intensity ratio between the lower/higher energy component, which we interpret as resulting from the energy difference between BE localized on ^{10}B/^{11}B, reflecting the 20/80 natural abundance ratio of these isotopes. This 1.34 μeV difference in BE localization energy agrees well with the prediction of Haynes Rule[7] in Si, together with the previously reported[6] 19 μeV difference in ionization energy between ^{10}B and ^{11}B acceptors seen in ^{28}Si. The narrowest observed B transition has a FWHM of $\sim$230 neV at $T=1.4$ K, increasing by almost a factor of 3 at 4.2 K. In spite of this strong temperature dependence, a comparison of the 1.4 K spectra from the three ^{28}Si samples with different isotopic enrichment strongly suggests that narrower B BE transitions could be observed in samples having an even higher isotopic enrichment.

We turn now to the P donor BE, which in the Shell Model[8] of BE and bound multiexciton complex structure in Si is expected to have a very simple, unsplit ground state. The single line observed[4] for the NP PL transition of the P BE in ^{nat}Si and ^{28}Si seemed to allow this prediction, but the

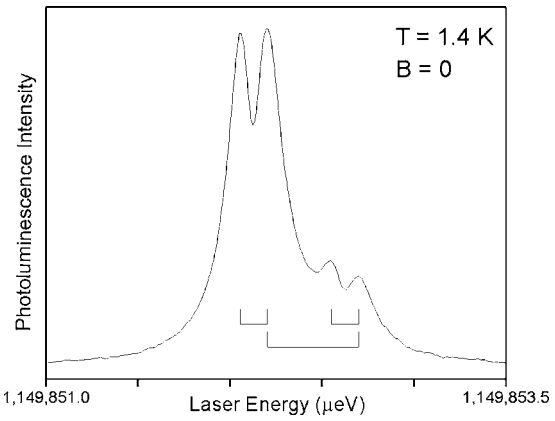

FIG. 2. A representative PLE spectrum of the NP P BE line in the ^{28}Si–*a* sample. The smaller splitting, indicated by the two small brackets, varies with excitation conditions, temperature, and sample purity. While the larger splitting remains constant, and is equal to the zero field hyperfine splitting of ^{31}P in Si.

new higher resolution PLE spectrum of the P BE in ^{28}Si shown in Fig. 2 is obviously more complicated. The two smaller splittings (indicated by the brackets) vary with temperature and the amount of above-gap excitation used to achieve photoneutralization, and are different between the different ^{28}Si samples, whereas the larger ~485 neV splitting remains constant. When this larger splitting is expressed in frequency units, 117 MHz, it is immediately recognized as the hyperfine splitting[5] of the P neutral donor ground state. The smaller, more variable splittings likely result from coupling between the P electron spin with the spins of other neutral impurities randomly placed around it. To test this hypothesis, a small magnetic field was applied to decouple these inter-impurity interactions, resulting in the spectrum shown in Fig. 3, which can be readily understood in terms of the Zeeman level diagram shown in Fig. 4. Note that at the fields and temperatures used here, all of the splittings are much less than kT. The electron and hole *g* factors determined from these spectra, $g_e = 1.97$, $g_{h(1/2)} = 0.83$, and $g_{h(3/2)} = 1.3$ are in good agreement with earlier studies[9] of the phosphorus bound exciton at much higher fields, and the sum of

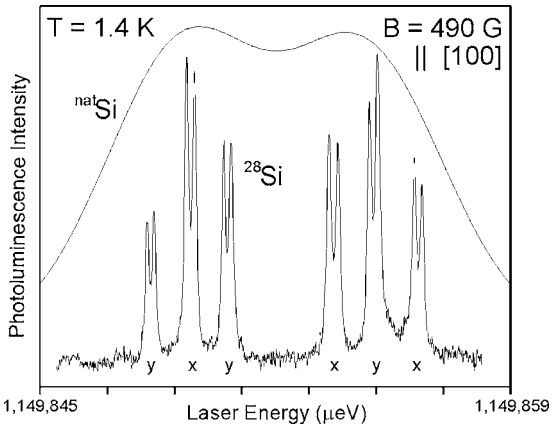

FIG. 3. The PLE spectrum of the P BE NP transitions in the ^{28}Si–*a* sample with a small applied magnetic field. The doublets labeled *x* and *y* arise from the hyperfine splitting of the donor ground state, as detailed in Fig. 4. For comparison the same spectrum is shown for ^{nat}Si, shifted to compensate for the difference in band gap energy.

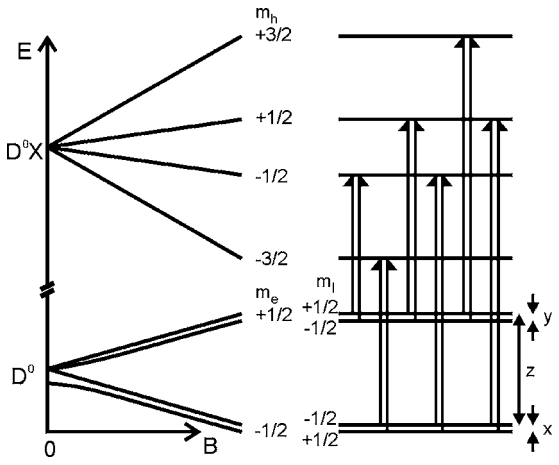

FIG. 4. A level diagram explaining the P BE transitions seen in Fig. 3. D^0 is the neutral donor ground state, which at zero field is split into a singlet and a triplet by the ~485 neV P hyperfine splitting. As a field is applied, the Zeeman splitting *z* resulting from the electron spin projection, m_e, grows, and the donor ground state transforms into two doublets, where the doublet splittings *x* and *y* depend on the projection of the nuclear spin, m_I, and at any field add to equal the zero field splitting. The two electrons in the BE ground state, D^0X, form a spin singlet, therefore, only the projection of the hole spin, m_h, affects the BE energy. There are six dipole allowed transitions between the two donor Zeeman levels and the four BE states, resulting in three *x* and three *y* doublets due to the donor hyperfine splitting.

the *x* and *y* hyperfine splittings agrees with the 486 neV (117.53 MHz) phosphorus donor hyperfine splitting determined by EPR.[5]

A fit to the 12 components seen in Fig. 3 gives an average FWHM of 150 neV, and a selectivity of 25 for one hyperfine state over the other when pumping at the peak of a subcomponent. The spectrum of the P BE in ^{nat}Si is also shown in Fig. 3 to emphasize the remarkable improvement in spectral resolution made possible by the near-elimination of the inhomogeneous isotope broadening present in ^{nat}Si. The 272 ns lifetime[10] of the phosphorus BE sets a lower limit of ~5 neV on the FWHM. While the homogeneous width may, in the future, be directly measurable. Next we show that ensemble linewidths, considerably lower than those demonstrated here, should be achievable in ^{28}Si samples having a higher enrichment. In Fig. 5 one of the hyperfine doublets shown in Fig. 3 is compared with that of the same sample at 4.2 K, as well as the 1.4 K spectra of the two other samples having a lower enrichment. The increase in temperature from 1.4 to 4.2 K produces only a 27% increase in linewidth, indicating that while temperature does play a role, it is not a major contributor to the low temperature linewidth. As compared to the well resolved splittings for the sample enriched to 99.991%, the hyperfine splitting is barely resolved for the sample with an enrichment of 99.983%, and is not resolved for the sample with 99.92% ^{28}Si.

These differences can be explained by a simple argument which assumes that inhomogeneous isotope broadening remains the dominant mechanism even at the highest enrichment studied here. Ignoring for simplicity the fact that the ratio of ^{29}Si and ^{30}Si may vary between natural Si and the enriched samples, the inhomogeneous isotope broadening will vary as the square root of 100% minus the enrichment (which for natural Si is 92.23%). The 5 μeV FWHM of the P

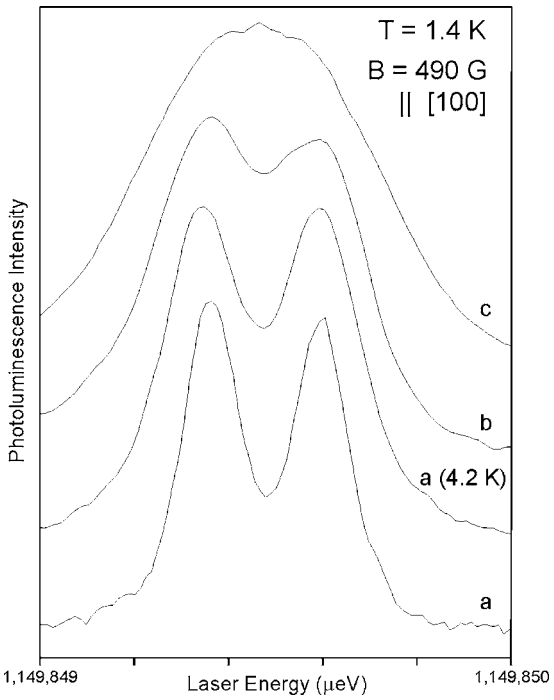

FIG. 5. Dependence of the P BE PLE line shapes on temperature and isotopic enrichment. At the bottom is a section of the spectrum of the sample enriched to 99.991% ^{28}Si shown in Fig. 3, while above it is a spectrum of the same sample at a temperature of 4.2 K [shifted up in energy to compensate for the temperature dependence of the band gap energy (Ref. 11)]. The spectrum labeled b is for a sample enriched to 99.983% ^{28}Si, and the spectrum labeled c is for a sample enriched to 99.92% ^{28}Si, both at 1.4 K.

BE in ^{nat}Si scales by this simple argument to widths of 510, 230, and 170 neV for the samples shown in Fig. 5, in order of increasing enrichment, in remarkably good agreement with what is observed. Ensemble linewidths, and certainly homogeneous linewidths, narrower than that reported here should, therefore, be achievable, together with hyperfine selectivity much larger than 25, in samples with a higher isotopic enrichment.

Due to the indirect band gap, shallow donor and acceptor BE in Si have very low radiative quantum efficiencies because of the dominance of nonradiative Auger recombination,[10] which is a drawback for optical detection of BEs as in PLE. For the P BE, the observed 272 ns lifetime is essentially equal to the Auger lifetime, since the radiative lifetime is ~2 ms.[10] However, it is possible to put the dominant Auger recombination to use by detecting the free electrons released in Auger recombination. In Fig. 6 we see the absorption spectrum of the phosphorus BE under conditions similar to those used in Fig. 3, as revealed by photocurrent spectroscopy rather than by PLE. Simple electrical contacts were made to the ends of the 2.5 cm long sample by rubbing on a thin layer of In-Ga eutectic, using fine copper wires to connect an external 1.5 V bias source and a transimpedance current amplifier. Strains generated by these simple contacts are likely responsible for the reduced resolution of Fig. 6 as compared to Fig. 3, but the hyperfine splittings are still clearly resolved.

IV. DISCUSSION

These results suggest a number of applications related to quantum computing and quantum information processing in

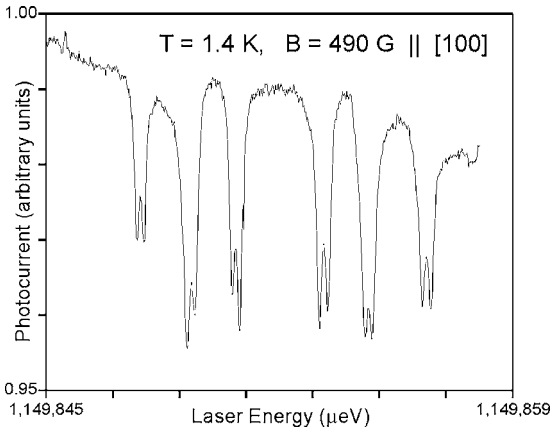

FIG. 6. Photocurrent spectroscopy of the phosphorus bound exciton transitions in sample ^{28}Si−*a*, with a magnetic field of 490 G applied parallel to the [100] axis. The photocurrent originates from the free electrons generated by the Auger decay of the resonantly created donor BE. Due to recombination, it appears as a reduction in the much larger nonresonant photocurrent due to holes released from the dominant impurity in this sample, the acceptor boron.

Si. Kane's[12] seminal proposal in which the nuclear spins of ^{31}P in Si could be used as an advantage, as qubits in quantum computation, led to many suggestions and modifications for the realization of this scheme. In particular related to the challenging problem of measuring the nuclear spin state. While many of these were based on Kane's[12] original idea of spin-to-charge conversion, others suggested approaches such as magnetic resonance force microscopy on single nuclear spins[13] or on ensembles of identical nuclear spins.[14] Based on our early results[4] of P BE linewidths in ^{28}Si, Fu *et al.*[15] suggested that it might be possible to detect the state of a single ^{31}P nuclear spin using the hyperfine splitting of the BE PL transition. However, this would have been quite difficult if the linewidths were as large as the ~620 neV upper limit set in the early study,[4] given that the hyperfine splitting of the BE transition was only ~243 neV. Our results, demonstrating ensemble linewidths of 150 neV and very well resolved hyperfine splittings in the BE transitions, demonstrate that this optical readout approach is indeed viable (note that the homogeneous linewidth for a single ^{31}P must be narrower than the ensemble linewidth, and that we have argued that reduced ensemble linewidths may be possible in a more highly enriched ^{28}Si).

One drawback of the optical readout scheme is the very low radiative quantum efficiency of these BEs, $\sim 10^{-4}$. We have demonstrated in Fig. 6 that the dominant Auger recombination channel can be used to our advantage in observing the BE spectrum, including the hyperfine splittings, via the photocurrent spectrum. This ability to resonantly ionize neutral ^{31}P donors in specific electronic and nuclear spin configurations suggests a potential readout mechanism for single nuclear spins: The optical-nuclear spin transistor. In this scheme the spin-selective Auger photoionization of a single neutral ^{31}P by the resonant creation of a BE would be detected by the resulting change in current in a nearby narrow channel field-effect transistor (FET) or single electron transistor.

The spin-selective creation of BEs and the resulting ion-

ization of the donors also suggests that it should be possible to achieve nuclear polarization, an important step in initializing a quantum computer, by dynamical optical pumping. Indeed, the results in Figs. 3 and 6 show that there is some polarization of the nuclear spins, even though the present experiment was in no way optimized to achieve such polarization. Another possibility is selective nuclear magnetic resonance (NMR), taking advantage of the fact that nuclear spin flip energies are very different for a neutral or an ionized ^{31}P donor (or donor BE, which should have spin flip energies very close to that of an ionized donor). Thus ^{31}P donors in selected electronic and nuclear spin states could be photoionized, and only these donors (or only the other donors) have their nuclear spins acted upon by an NMR pulse at the appropriate frequency. It should also be possible to optically address individual donors, or identical subsets of donors, within an inhomogeneous ensemble determined either by random perturbations (as in, for example, ^{nat}Si), or by a gradient in the magnetic field.

V. CONCLUSIONS

We have demonstrated the direct optical readout of the nuclear spin of ^{31}P impurities in ^{28}Si, and the selective ionization of donors in specific electronic and nuclear spin states, using the hyperfine splittings of the donor BE transitions. Possible applications of these results to quantum computing and information processing were discussed. Future possibilities are the observation of even narrower ensemble linewidths in a more highly enriched ^{28}Si, and the measurement of the homogeneous linewidth, either by hole burning or by the detection of the BE spectrum of a single ^{31}P. The achievement of a high nuclear polarization using optical pumping should be investigated, although this may require *n*-type samples to remove the need for the nonresonant excitation to achieve photoneutralization.

Many other optically accessible impurities and defects are known in Si, with widely different physical properties. For example, the high radiative quantum efficiency of isoelectronic BE may offer advantages in future quantum computing and information processing applications. Many of these centers may also reveal resolved hyperfine splittings once inhomogeneous broadening mechanisms are sufficiently reduced, and the properties of promising centers should, therefore, be re-examined in highly enriched ^{28}Si.

ACKNOWLEDGMENTS

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