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AUTHOR(S): R. B. Hammond and J. M. Meese

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Post Office Box 1663 Los Alamos, New Mexico 87545

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R. B. Hammond and J. M. Meese

Los Alamos Scientific Laboratory, Los Alamos, NM 87545
Missouri University Research Reactor, Columbia, MO 65201

INTRODUCTION

Crystalline Si, which is optically excited at low-temperature (~ 4 K), exhibits luminescence characteristic of several states for nonequilibrium electrons and holes. A single electron-hole pair can bind into an exciton that is chargeless but free to move in the lattice. Also, such a free exciton (FE) can become bound to a neutral impurity atom and become a bound exciton (BE). The energy of the BE state is lower than that of the FE by its binding energy to the impurity. An exciton will be bound to every type of neutral impurity atom with a different binding energy. Thus, when an electron-hole pair in a FE or BE state recombines radiatively, it emits a photon whose energy uniquely identifies the type of impurity atom to which it was bound or indicates that it was unbound. Recent work¹ has shown that an exciton luminescence spectrum from optically excited Si at ~ 4 K is a very sensitive indicator of the various types of dopant impurity atoms present in the crystal. More recent work² explained the kinetics of exciton capture and emission from impurity atoms and laid the ground work for making exciton luminescence a quantitative measure of impurity concentrations in Si. In this paper we, first, use the kinetics model of Hammond and Silver² to calculate the impurity concentration dependence of exciton luminescence intensities in Si and, second, report detailed measurements on NTD Si with known substitutional P concentrations. We show, first, the correctness of the kinetics model and, second, the practicality of exciton luminescence as a precise and extremely sensitive impurity diagnostic for Si.

Theory

Using the model of Hammond and Silver,² we can write

$$\frac{df_i}{dt} = \frac{f_i}{\tau_i} + \sigma_i \nu_{FE} n_{FE} - f_i \sigma_i \nu_{FE} \frac{AT^{3/2}}{g_i} [1 + \exp(-\Delta E/T)] \exp(-E_i/T)$$

where f_i is the fraction of type i impurity atoms that hold a BE, τ_i is the recombination lifetime of an exciton bound to a type i impurity, σ_i is the capture cross section for an exciton at a type i impurity, ν_{FE} is the FE thermal velocity, n_{FE} is the FE density, A is the density of states factor for FE's, T is the absolute temperature, g_i is a BE degeneracy factor, ΔE is the FE ground-state splitting 0.31 meV (Ref. 3), and E_i is the binding energy of an exciton bound to a type i impurity. This equation holds when $f_i \ll 1$.

If we now assume that the Si crystal is excited with a continuous optical source (dc excitation), $df_i/dt = 0$, and

$$\frac{f_i}{n_{FE}} = \frac{\tau_i \sigma_i \nu_{FE}}{1 + \tau_i \sigma_i \frac{AT^{3/2}}{g_i} [1 + \exp(-\Delta E/T)] \exp(-E_i/T)}$$

The important aspect of this equation is that the right-hand side depends only on the type of impurity atom, i , and on the absolute temperature. We draw three major conclusions from this fact. First, the ratio $(n f_i / n_{FE})$ of excitons bound to type i impurities to FE's is independent of other types of impurities in the crystal. Second, this ratio is independent of the FE lifetime (a poorly understood and highly variable quantity). Third, this ratio is directly proportional to the concentration of type i impurity atoms if we assume a constant temperature.

Experimentally we can measure the ratio of BE to FE luminescence intensity. This measurable ratio is proportional to the ratio $n f_i / n_{FE}$. Thus, if we measure BE to FE luminescence intensity ratios at low excitation (that is, $f_i \ll 1$) and at fixed temperature we should find the results depend only on impurity concentration n_i and are directly proportional to impurity concentration.

Experimental

In this study we used 15 NTD Si samples doped in the range from $2 \times 10^{11} \text{ cm}^{-3}$ to $2 \times 10^{16} \text{ cm}^{-3}$. Each of the samples contained $\sim 1 \times 10^{13} \text{ cm}^{-3}$ B. The P doping concentrations were either calculated from neutron dose, from measured resistivity, or from Hall effect results. The crystals were chemically etched on all surfaces. They were immersed in LHe at 3.96 K and irradiated with a

calibrated GaAs LED. The luminescence was analyzed with a SPEX 1702 3/4-m grating spectrometer and detected with an RCA 7102 S-1 photomultiplier operated at 77 K in the photon counting mode. The spectrometer broadening was 0.43 meV at 1.1503 eV and 0.39 meV at 1.0972 eV FWHM. Ratios were taken of the peak intensities of the P no-phonon-assisted BE luminescence at 1.1503 eV to the TO-phonon-assisted FE luminescence at 1.0972 eV.

Results

With optical excitation intensity below ~ 50 mW/cm² we found, first, that no P-bound multiexciton complex lines were observed and, second, that the ratio of BE-to-FE luminescence intensities was independent of excitation intensity. This confirmed that below ~ 50 mW/cm² at 3.96 K, our assumption $f_1 \ll 1$ was valid. In order to have a safe margin for error we took all our data for this work at 3.6 mW/cm². Figure 1 shows representative FE and BE spectra taken under these conditions. Figure 2 shows the results of our measurements of P BE-to-FE luminescence intensity ratios plotted versus substitutional P concentration. The results show the proportionality predicted by the kinetics model over 4 orders of magnitude in impurity concentration. The standard deviation of these data from the proportionality is 7%. We found that the samples, which were more carefully characterized for P content, have less deviation from the precise proportionality. In general, the deviations reflect the accuracy with which the actual P concentrations were known for these crystals.

Conclusions

First, we have shown that at a fixed temperature of 3.96 K, BE/FE ratios are directly proportional to P concentration in NTD Si. Second, we have also shown that a variation from 0.75 μ s to 30 μ s for FE lifetime in our samples did not affect this result. Thus, we have confirmed the major predictions of the theory and established an extremely sensitive and accurate impurity diagnostic for NTD Si.

Our experimental arrangement gives us a sensitivity to $\sim 1 \times 10^8$ cm⁻³ P. Also, once the experiment is operating, a single sample may be measured and the P concentration calculated in approximately 15 minutes. We normally use 1-cm² samples about 0.05 cm thick. The extreme sensitivity of this method suggests its use for very small samples and for impurity profiling of samples.

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Fig. 1. Photoluminescence spectra taken at 3.96 K with an optical excitation of 9 mW/cm². The P no-phonon-assisted BE luminescence at 1.0776 μm and the FE to-phonon-assisted luminescence are shown. The P content of this crystal was 9×10^{16} cm⁻³.

Fig. 2. Ratios of the intensities of the P NO-phonon BE luminescence peak at 1.1503 eV to the FE TO-phonon luminescence peak at 1.0972 eV are plotted vs P concentration. Results from 15 NTD Si samples are shown. Data were taken in the low-excitation regime at 3.96 K. Spectrometer broadening was 4 Å FWHM. Optical excitation intensity was 3.6 mW/ cm^2 . All 15 samples contain $\sim 1 \times 10^{12} \text{ cm}^{-3}$ B. The line through the data corresponds to $n_p = 4.5 \times 10^{12} \text{ cm}^{-3}$ (p^{NP} / F^{TO}). The data fit the line with a standard deviation of 7%.