ELECTRONIC RAMAN SCATTERING OF DONOR ATOMS IN SILICON: APPLICATIONS TO QUANTUM COMPUTING

S. Prawer, N. Stavrias, P. G. Spizzirri and D. N. Jamieson.

Centre of Excellence for Quantum Computer Technology, School of Physics, University of Melbourne, Australia. E-Mail: s.prawer@unimelb.edu.au

Keywords: wavefunction overlap, quantum computer, electronic Raman scattering.

Abstract: Development of a quantum computer capable of massively parallel computation is one of the most important scientific and technological goals of this century. The Australian Centre of Excellence for Quantum Computer Technology is attempting to construct a quantum computer whose operational elements (i.e. qubits) are single phosphorus donor atoms placed with atomic precision in a silicon matrix. This paper reports on the application of electronic Raman scattering (ERS) and photoluminescence (PL) techniques to the fabrication of such a solid-state quantum computing (QC) device. ERS has the potential to provide a direct measure of the degree of overlap of the donor wavefunctions, knowledge of which is crucial to the successful operation of a solid state quantum computer.

Introduction

In the Kane realisation [1] of a solid state quantum computer, individual phosphorous donor atoms are placed with high precision and in close proximity just below the surface of a silicon substrate as shown in Figure 1. Here, the phosphorous nuclear spins act as quantum bits (qubits) in either “spin up” (i.e. binary 1) or “spin down” (i.e. binary 0) states. Electrons mediate interactions between the nuclear spins because they are mobile and can be controlled by externally applied electric fields through control gates above them. Readout of the qubit spin state through single electron spin measurement has been proposed although other schemes are also being investigated.

Figure 1. The Kane proposal for a silicon based quantum computer using phosphorous nuclear states as qubits.

Crucial to the operation of this device is controlled electronic wavefunction overlap, a prerequisite to donor entanglement and quantum computer operation. Thus, a critical milestone in the fabrication process is to establish that wavefunction overlap has been achieved using one of the atomic placement strategies employed. Recently, an optical method capable of estimating the
strength of wavefunction overlap between neighbouring phosphorous donors in silicon has been proposed [2]. Based upon electronic Raman scattering (ERS), the technique proposed can provide a direct measure of the exchange coupling constant (J).

**Donor Spectroscopy**

Silicon is an indirect bandgap material with a multi-valley conduction band (i.e. 6 degenerate minima) at zero wave vector. As a result of the valley-orbit coupling among states associated with the various equivalent conduction band minima, the degenerate donor ground state splits into the lowest donor-electron energy states which are a: 1s(A_1) ground-state singlet, an excited triplet 1s(T_2) and a doublet 1s(E) state; consistent with the T_d point group site symmetry of the impurity atom. While valley orbit transitions of 1s(A_1) → 1s(E) states for single donors are forbidden in absorption by the selection rules, they have been observed using the technique of electronic Raman scattering (ERS) (but note that the single donor 1s(A_1) → 1s(T_2) transition is not Raman active). First reported by Wright et al [3] and later studied by Jain et al [4], the Si:P 1s(A_1) → 1s(E) transitions were shown to be very sensitive to the donor environment (e.g. strain fields, ionised pairs or surface charge) [2] and concentration [4].

These valley orbit transitions are most commonly observed using ERS and their large cross sections are believed to be due to the presence of many valley conduction bands [5]. It can therefore be used to study low lying levels with the same parity as the ground state (see figure 2). This is in contrast to the usual Raman effect that is associated with the excitation or de-excitation of vibrational quanta. An energy diagram for the Si:P system is shown in Figure 2 where a comparison of conventional near infra-red (NIR) absorption and ERS is illustrated.

![Energy Level diagram for P in Si](image)

**Figure 2.** Spectroscopy of phosphorous in silicon [5].
Donor – Donor Interactions

A result of inter-donor interaction is that donor pair states are perturbed. Originally observed as an asymmetric broadening with increasing donor concentration [4], the valley orbit transition eventually disappears into a continuous background. This has been explained theoretically by Koiller et al [2] who have calculated the energies and Raman intensities of each of the donor pair states as shown in Figure 3. An estimate of the exchange coupling constant (J), the parameter of interest, can be derived from plot (b) at the intersection of the singlet and triplet intensity curves.

![Figure 3](image)

Figure 3. (a) Raman shifts for a pair of donors showing splitting of the singlet and triplet transitions with donor separation and (b) the temperature dependence of Raman line intensities for an impurity pair with exchange coupling [2].

It is clear from Figure 3(b) that accurate measurements of the sample temperature in the measurement volume, whilst working at liquid helium temperatures, is required. This problem can be addressed using Raman spectroscopy in one of two ways. Commonly, the stokes and anti-stokes intensity ratio of the first order silicon TO phonon is determined from which the sample temperature can be estimated. In comparison, a single stokes measurement of the same spectral feature, which exhibits temperature dependent shifts, can yield the same information. A calibration plot obtained under high spectral and spatial resolution is shown in Figure 4. The advantage of using Raman spectroscopy for temperature measurement in this instance is that the determination is from the same sample micro-volume under analysis and it is a concurrent, non-contact measurement. A theoretical trendline [6] is also shown with the calibration curve however it is clear that it does not describe the measured behaviour below approximately 50K, the Debye temperature for silicon.
Samples

In semiconductors, a reduced donor separation (i.e. increased wavefunction overlap) can be achieved through higher doping levels. By adjusting the donor concentration, the electron-electron interaction can be studied up to the limiting metal insulator or Mott transition [7] where the material becomes metallic with delocalised states. It is at this point that a continuous scattering background arises from delocalised Fermi electrons as originally observed by Jain [4]. Avoiding the MOTT transition is therefore essential to quantum computer operation however, achieving the inter-donor separations required for spectral resolution shown in plot 3(a) is problematic. Conventional implantation or bulk doping techniques would result in metallic states at these donor separations so an alternative approach is needed.

An ion implantation approach can be employed to dope the silicon wafer to any desired P concentration however, increasing the implantation dose to decrease the donor-donor separation can lead to P concentrations exceeding the metal insulator transition (MOTT). A variation of the implantation approach which overcomes this limitation, called molecular beam implantation, is proposed that could provide better control over the interdonor and interpair spacing. The technique uses atomic pairs (molecules) or clusters of atoms, instead of individual ions, that dissociate upon impact/entry into the substrate. The resulting straggling processes leave the ion pair within close proximity. For comparison, conventional doping or implanting techniques effect a statistical distribution of donors whereas molecular beam implantation provides the ability to control donor pair and inter-pair separation simply by tuning the implantation energy. A summary of the differences between the two implantation strategies is illustrated in Figure 5, based on molecular dynamics and Monte-Carlo simulations.
Raman and Photoluminescence

The discussion thus far has centred on using Raman techniques to probe the electronic environment of donor states in silicon. An alternative approach is to use photoluminescence (PL) which is inherently more sensitive than scattering, a result of small scattering cross sections [10]. For semiconductors systems like P in Si, PL is usually the result of exciton formation. Arising from the generation of electron-hole pairs formed following absorption of sub-bandgap excitation, relaxation is mediated by two processes: (i) scattering with a large number of phonons or (ii) radiative recombination (i.e. PL).

While scattering and PL are generally considered distinct processes, at energies close to the bandgap, this distinction may become blurred. For example in work by Yu et al [9] with CdSe, the excitation frequency dependence of the “emission” frequency exhibits scattering like behaviour close to the bandgap and PL like behaviour further from the bandgap. Even for simple systems, it is possible to confuse Raman and PL signals close to the bandgap.

When Raman and PL are used in combination, a type of “quantum counter” can be established providing a direct measure of the PL quantum yield. As excitons are easily influenced by other charged ions or traps, their recombination yields will reflect their electronic environment whereas the scattering cross sections will not be influenced. An example of this is shown in Figure 6 below from the work of Broussel [10] where the combined scattering and emission spectra are normalised for the free exciton (FE) signal. While the unnormalised spectra appear very similar, the absence of dislocation peaks (D_1 – D_4) in spectrum (a) is direct evidence of dislocation free material. The higher FE PL quantum efficiency can therefore be correlated with dislocation free material without the need to examine the entire spectral range shown. Finally, it is clear that while PL is an important tool for studying semiconductors, the combination of Raman and PL provides a wealth of information not readily obtained using any other technique.

Figure 5. Illustration of the molecular implantation strategy for donor pair placement.
Figure 6. Raman and luminescence spectra from ultrapure silicon that is (a) dislocation free and (b) with dislocations. The Raman line at ~9023 cm⁻¹ reveals the relative intensity ratio of the free exciton emission. Dislocation peaks (D lines) are also evident at lower energies.

Acknowledgements:
This work was supported by the Australian Research Council and the USA Army Research Office under contract number DAAD19-01-1-0653.

References