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High Resolution optical spectroscopy in isotopically-pure Si using radioactive isotopes: towards a re-evaluation of deep centres

Mike Thewalt¹, Karl Johnston^{2a}, Martin Henry³¹Dept of Physics, Simon Fraser University, Burnaby, British Columbia, Canada, V5A 1S6²PH Dept, CERN, 1211 Geneva 23³School of Physical Sciences, Dublin City University, Glasnevin, Dublin 9, Ireland^aSpokesperson and Contact Person at ISOLDE

Abstract

Deep centres in silicon have been studied in great detail over the last 50 years and much progress has been made in the understanding and control of impurities in this material. Much of this effort has been focussed on the problems of metallic impurities such as Fe, Ag, Cu and Au. These are impurities that diffuse quickly into the crystal and hamper device performance. Although the understanding of these impurity centres in Si is widely thought to be “solved” recent experiments with isotopically-pure Si are disproving long-held results and are opening up new perspectives on the constituent nature of deep centres in Si. In particular, there is new evidence to show that the family of Cu, Ag and Au may all show essentially the same behaviour by forming a cluster of *any four atoms* of these elements. This has been established for Cu and Ag through the use of different stable isotopes in the preparation of samples, but the case of Au remains unproven since there is only one stable Au isotope. In this proposal we aim to address the only remaining unknown regarding this remarkable behaviour through the use of the radioactive isotope ¹⁹⁵Hg in conjunction with stable ¹⁹⁷Au. This proposal may also be the precursor to a more detailed examination of deep centres in this and other materials using high-resolution spectroscopy in combination with isotopically-enriched materials.

Introduction

Silicon is the pre-eminent semiconductor and is likely to remain so for the foreseeable future (1). It is the basis for at least 90% of the information technology that we see around us today. In spite of its shortcomings as an optical and high-speed material, it still underpins the microprocessor industry and continues to develop as with the recent move by Intel to 45nm technology incorporating Hf-based high-k dielectrics (2), and the development of a silicon-based laser for optical interconnects (3)

The path to such widespread application of Si involved extensive study from the dawn of silicon technology in the 1950s. Among the most difficult problems that had to be overcome was the control of impurities, detrimental to device performance, which diffuse readily through Si at the high temperatures used in manufacturing. A case in point is Cu; this diffuses so quickly into Si that it is almost impossible to eliminate from the processing of the material. For example, at 900°C the diffusion coefficient is $\sim 5 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ which is about 7 orders of magnitude greater than that of oxygen (4). With such high diffusivities it is extremely difficult, verging on the impossible, to eliminate this impurity from the bulk crystal and as a consequence trace amounts are nearly always present. Other fast-diffusers are metals such as Fe, Ag and Au – and detailed study over several decades has enabled technological problems associated with these to be largely overcome. However, the scientific understanding of these impurities has been thrown wide open by recent research using photoluminescence spectroscopy on isotopically enriched silicon.

Optical Spectroscopy of semiconductors

One of the techniques most commonly used to characterise impurities in semiconductors is Photoluminescence (PL). This is a non-destructive spectroscopy that characterises the optical properties of a material. The most common way of generating luminescence in semiconductors is to use an optical pump (usually a laser) to produce electrons and holes in the semiconductor. The term photoluminescence is used to denote such optically generated luminescence. When these carriers become bound at defects or impurities and recombine with holes or electrons respectively, photons with energies related

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to the energy level of the defect in the band gap are emitted. Features like the spectrum of the recombination energies, the vibrational side bands, and temperature dependence of the intensities, contain a great wealth of information on defects or impurities. PL is employed widely in all classes of semiconductor research and is recognized as one of the most important and powerful techniques available (5). The principal advantage is, in addition to the usual advantages pertaining to spectroscopy, the potential for very high sensitivity. For semiconductors, the penetration depth of the laser radiation and the diffusion length of electrons and holes are generally of the order of 100 nm, often less. Depending on the recombination process, the detection limit can be as low as 10^{13} cm^{-3} in favourable cases, so that a total of 10^9 atoms can be sufficient to produce detectable PL signals. To get the full benefits from PL it is usually necessary to operate at liquid helium temperatures to freeze out all thermally excited charge carriers. At these temperatures even weakly bound electrons and holes remain bound at defects/impurities so that the optical transitions occur and vibrational (phononic) effects are minimized. One consequence of this high sensitivity is the capability of detecting trace contaminants in nominally intrinsic semiconductors.

Due to its high sensitivity and the wealth of different PL signals, the assignment of the different signals to a particular defect is often a puzzle. In semiconductors with residual impurities below the threshold concentration for PL detection intentional doping and its correlation to the intensity of PL transitions is used to identify the chemical nature of defect levels. In this way many defect levels in Si, Ge, and GaAs have been identified over recent decades. In general, an unambiguous chemical identification of a defect level is provided only by the observation of an element specific property, like the isotope mass, the nuclear spin, or the isotope abundance.

If light impurities are involved in the defect one can usually observe the isotope shift of no-phonon lines or local mode phonon replicas (6). Another possibility exists in the determination of the hyperfine interaction by electron paramagnetic resonance (EPR) or electron-nuclear double resonance (ENDOR) experiments where selective photo-excitation or photo-ionization of a paramagnetic level helps to determine the defect level (7). These two methods, however, require a paramagnetic level, suitable nuclear properties of the involved elements, and a control over the Fermi-level for selective photo-excitation. Due to these limitations, the use of the nuclear lifetime of a radioactive isotope undergoing a chemical transmutation has become a most versatile tool for identifying defect levels. If the level is caused by a defect in which the parent or daughter isotope is involved the concentration of that defect will change with the characteristic time constant of the radioactive decay. The first successful application of this technique was demonstrated in 1965 by I. Broser and K.-H. Franke (8) who doped ZnS homogeneously with radioactive ^{65}Zn by neutron irradiation. Due to the decay of ^{65}Zn to ^{65}Cu they were able to determine the defect level of Cu in ZnS. It took about 25 years until this type of PL experiment was reinvented by several groups to identify defect states in Si (9), GaAs (10), GaN (11), and ZnO (12). In all these experiments ion implantation was used for doping with radioactive isotopes.

Optical Spectroscopy of single-isotope Si

Si is present naturally in the form of three isotopes: ^{28}Si (92.223 %), ^{29}Si (4.685 %) and ^{30}Si (3.092 %). Therefore it might be thought that as it is naturally 92% mono-isotopic, there would be little to benefit by moving to the purely ^{28}Si material. In fact the exact opposite is found to be the case. Even though very good quality single crystal had been studied for many years using optical spectroscopy, the move to isotopically-enriched material proved to have a dramatic effect, due to the reduction in stress that this brings about. Recent work by Thewalt and co-workers (13; 14; 15) shows that optical features sharpen up by more than an order of magnitude when the single isotope is used, and this allows a wealth of new and surprising data to be obtained about centres long-thought to be understood. We will summarise some of this work as a prelude to the request specific to this proposal.

To take an example, as mentioned in the introduction, the transition metal Cu has a very fast diffusion coefficient in Si. This results in its being a difficult to understand yet omnipresent impurity in Si and as a result has resulted in some controversy over the years. What is well-established is that Cu gives rise to an optical transition with a zero-phonon(ZPL) line at 1014 meV (16). In addition, there is a vibronic sideband with quanta of 7, 16.4 and 25.1 meV which results in the relatively complex spectrum as seen in Figure 1.

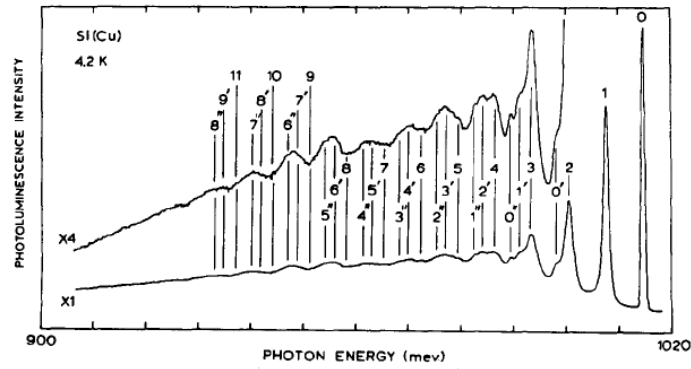


Figure 1 Photoluminescence spectrum of the Cu-related band with ZPL at 1014 meV. Phonon progressions are denoted by 0, 1, 2 ... etc (taken from Davies, 1989 (16)).

There have been many papers on the 1014 Cu band in Si due to the importance of Cu in Si technology and a common concern is the number of Cu atoms which give rise to the luminescence (17; 18; 19). The experimental work of Weber *et al.* (17) using selective Cu isotope implantation led to a general acceptance that the defect producing the 1014meV luminescence consists of a Cu pair. This model was supported by theoretical calculations showing that a substitutional-interstitial ($\text{Cu}_s\text{-Cu}_i$) pair would account for the properties of the centre (20). However others continue to argue for a single Cu centre (18).

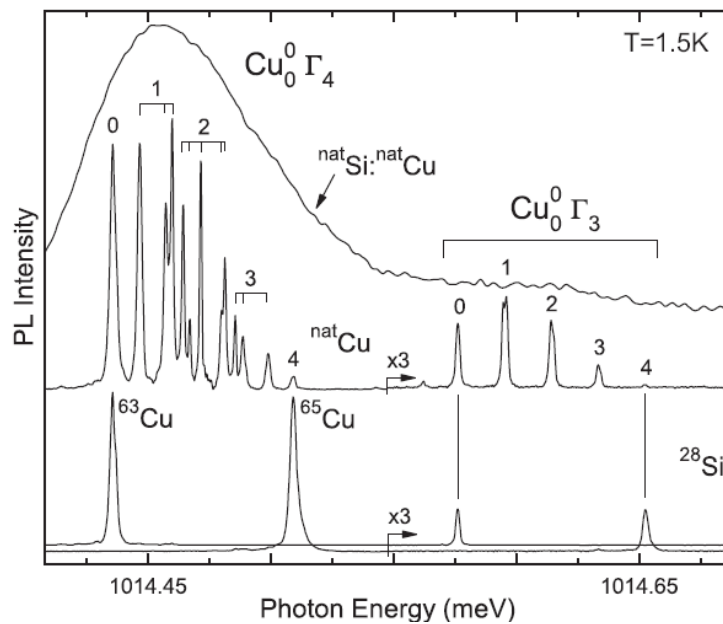


Figure 2 The dramatic effect of replacing natSi with ^{28}Si is seen. The upper spectrum shows the feature seen in Figure 1, the ZPL at 1014meV. The lower two spectra are of the same feature in ^{28}Si in two different configurations. The first when natCu is diffused into the sample; the second when enriched ^{63}Cu or ^{65}Cu are introduced. As can be seen the wealth of new structure is considerable.

The use of isotopically enriched Si has opened up all of this again. The dramatic effect of replacing natural Si with mono-isotopic can be seen in Figure 2; the single feature seen in Figure 1 now becomes a host of different and very sharp lines. Indeed the optical features that arise from single-isotope material are often so sharp that they go beyond the instrumental resolution currently available which, at the current state-of-the-art is $\sim 0.014 \text{ cm}^{-1}$ (21). This is from recent work by Thewalt *et al.* (14) whereby different concentrations of Cu were introduced into the silicon by a diffusion process and the full results are discussed in detail in that paper. In short, the results of Figure 2 cannot be explained by only a pair of Cu atoms, and appear to be only properly described by invoking at least 4 Cu atoms in the centre. This is a very surprising result, given that the Cu-pair model appeared to account for many of the properties of this optical centre. Equally significantly, there is evidence from the research that any four atoms of Cu and Ag will produce a luminescence centre, and it suggests that there is a stability associated with such 4-atom-containing centres that is as yet not explained theoretically. It indicates that there may in fact be whole families of semiconductor impurity centres which are comprised of more impurity atoms than expected but which have remained undiscovered and unstudied, due to the broadening of spectral lines in multi-isotopic material. This proposal hopes to pursue these questions in more detail in the first instance by focussing on the behaviour of Au in Si.

Background to the proposed experiments

Au in Si is perhaps the most-studied of all the deep donors and is known to have an optical feature at 793 meV (16). This has been suggested to be associated with a deep Au donor, but Au is known to display amphoteric behaviour i.e. acting as a donor or as an acceptor. As such it is ripe for re-evaluation and it has been suggested that the centre is fact a Au₄ complex, showing similar behaviour to the Cu₄ centre discussed above (13). However, Au has only one stable isotope – ¹⁹⁷Au – and it is by careful examination of the spectra using different stable isotope impurities that have enabled the results on Cu to be obtained. Therefore one solution is to implant with a long-lived radioactive isotope, in this case ¹⁹⁵Au, to see if an effect can be seen. This has the twin possibility of being able to measure a mass isotope shift and also to see a drop or change in intensity in the optical spectrum as the radioactive Au decays.

Proposed Experiments:

The proposed experiments are for collections of ¹⁹⁵Hg and/or ¹⁹⁵Pb which ultimately decay into the required isotope of ¹⁹⁵Au, which has a half-life of 181 days. The likely dose would be approximately 3.10¹¹ atoms collected through a 5x5mm² collimator, which translates to a dose of 10¹² cm⁻². The targets required would be UCx with RILIS for the ¹⁹⁵Pb or molten Pb with a plasma ion source for the ¹⁹⁵Hg. The length of time to make such a collection would be about 3-4 hours based on the yield information in the ISOLDE database. Collections will be best performed at the GLM, due to the greater control and focussing of the beam that can be obtained there. However, the collections can also be performed at the high voltage platform if the target were to be placed on the HRS. The accelerating voltage required would be 60kV or less.

The samples will thereafter be stored at ISOLDE until the Au is produced and then shipped to Simon-Fraser University in Canada. The needs from ISOLDE are minimal. Some basic cleaning and mounting will be performed of the samples in building 115, but essentially only the collections will be performed here. A shipping agreement between CERN and Simon-Fraser University is required, but this will be sorted out well before the beam time.

We intend to make a number of samples. Some will be collections into pure ²⁸Si whilst there will also be some Si samples pre-implanted/diffused with ¹⁹⁷Au to see if isotope shifts can be seen. In total we would like to make between **4-6** samples and therefore request **6** shifts to allow for tuning and setup.

Table 1 Requested isotopes for the current proposal

Isotope	Half-life	Implantation energy (keV)	Target	Ion Source
¹⁹⁵Hg/¹⁹⁵Au	40h/186d	60 (or less)	Molten Pb	Plasma
¹⁹⁵Pb→ ¹⁹⁵Au	15m / 186d	60 (or less)	UCx	RILIS

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