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LETTER TO THE EDITOR

Radioactive isotopes for photoluminescence spectroscopy—^{111}In in silicon

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Abstract. A sample of high-purity silicon was implanted with the radioactive isotope ^{111}In ($\tau_{1/2}$ = 2.8 d) to a total dose of 10^{11} atoms. The sample was rapidly thermally annealed and quenched to room temperature. The intense photoluminescence (PL) characteristic of Si:In (labelled PQR) produced by this treatment was found to decay non-exponentially and much faster than expected for the ^{111}In half-life. The intensity of the neutral In acceptor bound exciton PL, on the other hand, decays roughly as expected. New features appear in the spectrum over periods of days and weeks. Although none of these can be directly attributed to daughter centres of the In PQR or substitutional acceptor centres, they are believed to be due to Cd impurities produced in the radioactive decay. A complex line structure and temperature dependence is observed for the new spectra. These results confirm the feasibility of using radioactive isotopes in PL spectroscopy, and they illustrate the power of the technique for defect analysis.

Radioactive isotopes have had a relatively narrow range of applications in semiconductor research, which is hardly surprising given the difficulties associated with their production and handling. The principal application has been in diffusion studies where the penetration of the atoms into a solid can be accurately measured using conventional counting techniques [1]. Mössbauer spectroscopy has been a consistent feature of semiconductor research, albeit with a limited number of suitable isotopes [2]. A relative newcomer to semiconductor spectroscopy is perturbed angular correlation (PAC) in which the details of γ-ray emission are used to provide information on defect characteristics [3]. This, too, suffers from the limited availability of suitable γ emitters. Lastly, the channelling and blocking of radioactive decay products can be used to reveal information regarding the location of impurities in crystals [4].

All of these techniques are unified by the fact that the decay products (radiation or particles) are monitored directly. This limitation need not apply—the effect of a radioactive decay process on other signatures of the isotope or its daughter products can be exploited. In the case of semiconductors, this was first demonstrated by Petersen and Nielsen [5] in a DLTS study of gold- and platinum-related defects in Si. Other DLTS studies followed, confirming the feasibility of the technique [6]. The appearance or disappearance of a spectrum at a rate consistent with a specific radioactive half-life can thus provide excellent information on the chemical identity of defect impurities. In this letter we report the results of a photoluminescence (PL) study of silicon implanted with the radioactive isotope ^{111}In. There are several reasons for choosing this isotope. Firstly, the half-life of 2.8 d is suitable for

the practicalities of PL spectroscopy. Secondly, In in silicon is known to produce one of the most intense PL emissions recorded for silicon (when suitably treated [7, 8]) so that a low dose implantation, and hence low activity, suffices. The experiment not only confirms the feasibility of the technique, it also provides surprising new data on the Si:In PL properties and reveals new PL spectra which are assigned to Cd defects produced in the decay of the implanted ^{111}In isotope. This is the first report of Cd-related photoluminescence in silicon.

The starting material used was from a high-purity floating-zone silicon ingot with a resistivity of approximately 20000 Ω cm. Radioactive ^{111}In ions were implanted at an energy of 80 keV to a total dose of 10^{11} atoms into an area of (2×2) mm^2. The measured activity of the sample followed implantation was 10 μCi. The sample was RCA cleaned and a rapid thermal annealing process was performed in air in the manner described by Thewalt *et al* [7] to enhance the Si:In PL. A Bomen DA8 FT spectrometer fitted with a North Coast Ge detector was used to record the PL spectra. An air cooled argon ion laser operating at 100 mW was used to excite the luminescence. The sample was placed in a CF1204 Oxford Instruments helium flow cryostat. Notwithstanding the low activity of the sample, lead shielding was used around the cryostat except for areas of optical access.

For samples produced by ion implantation, the implanted ion reside in a thin layer just below the surface. The range and straggle are only ~45 nm and 13 nm, respectively, for the case discussed here. Accordingly, the PL emission includes contributions from surrounding regions of the sample which are excited by the laser excitation. These contributions take the form of free exciton and boron bound exciton recombination, boron being the residual impurity in the sample. This becomes evident in the data presented below.

Before describing the results below it is necessary to point out some distinctive features of practical PL spectroscopy. The technique is particularly well suited, due to its high sensitivity, to situations involving low concentrations or small volumes. However, a disadvantage is the difficulty of producing quantitative intensity data, an important consideration for the experiment described here. This is particularly true when excitation is achieved by using radiation with energy greater than the band gap energy. The intensity of a defect PL spectrum then depends critically on the capture cross section of the defect for excitons or free electrons and holes, and on the radiative efficiency of the defect following the capture process. Competition between centres for the free carriers and/or excitons may result in only one defect dominating the spectrum; the appearance of a new spectrum for different conditions may result simply from the elimination of totally unrelated but much more effective carrier traps. The concentration of a defect is also a key factor. For low concentrations, it is possible to saturate a PL line intensity, i.e. increasing the excitation density cannot produce greater PL intensity since all available defects are excited. However, if the defect concentration is high, it may not be possible to achieve saturation. Aside from all of these fundamental considerations, the requirement of reproducible optical and temperature conditions must be met for quantitative measurements. These and other issues relevant to PL spectroscopy are discussed in detail by Lightowlers [9].

To illustrate the situation for the results presented here, a PL spectrum of Si:In recorded at 5.5 K is shown in figure 1(a). The line at ~9200 cm^{-1} is due to neutral In acceptor bound exciton (BE) recombination. The line at 9013 cm^{-1} is the P line of the In-related 'PQR' spectrum [10]. The asymmetric feature at ~ 8850 cm^{-1} is due to free exciton recombination with the emission of LO or TO phonons, and the line at ~8815 cm^{-1} is due to BE recombination at neutral boron acceptors, again with the emission of TO phonons. The effects of different excitation conditions are shown in figure 1(b). When the laser power is increased from 80 mW neither the boron-related line nor the P line changes appreciably in intensity. However, the intensities of both the In acceptor BE line and the free exciton

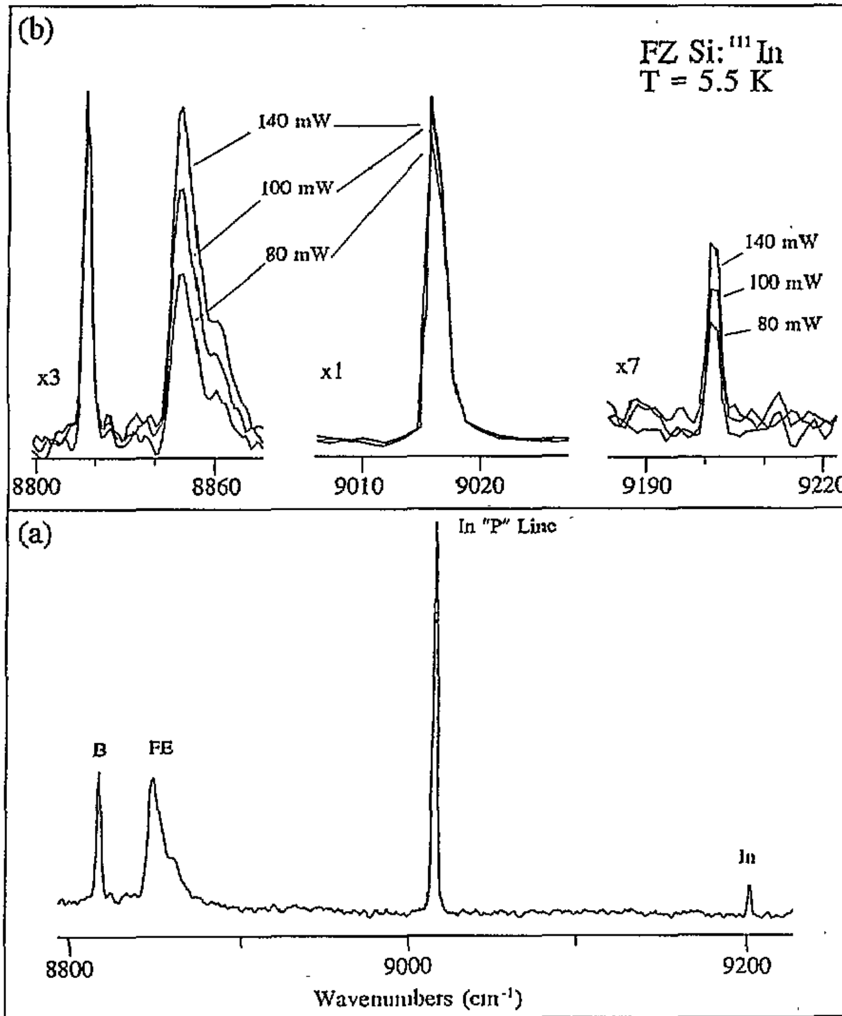

Figure 1. (a) The PL spectrum of Si:In recorded at 5.5 K and for a laser power of 140 mW. (b) Spectra recorded at 5.5 K for laser powers of 80, 100 and 140 mW.

line increase with laser power. Hence, the PQR and boron PL intensities are saturated, whereas the neutral In acceptor PL is not. The boron concentration is known to be low, less than 10^{13} cm^{-3}. The total In concentration following implantation is estimated to be $\sim 6\times10^{17}$ cm^{-3}. The rapid thermal anneal does not alter this significantly. We can conclude that only a small fraction of the implanted In is involved in the PQR centres in agreement with Thewalt *et al* [7]. The choice of laser power is clearly very important for comparing PL line intensities. In the data described below, we examine the intensity of the P line and the indium acceptor BE line as a function of time. We chose a laser power of 100 mW as standard for the experiment since this was sufficient to achieve saturation of the P line when the PQR centre concentration was at its greatest value; with the concentration expected to decrease with time this condition would be maintained. For the indium acceptor BE we could not achieve this condition. Here, the only danger was that the PL might become saturated as the indium concentration decreased with time. However, care was taken to

ensure that this possibility was not overlooked in the experiment by recording spectra over a range of laser powers.

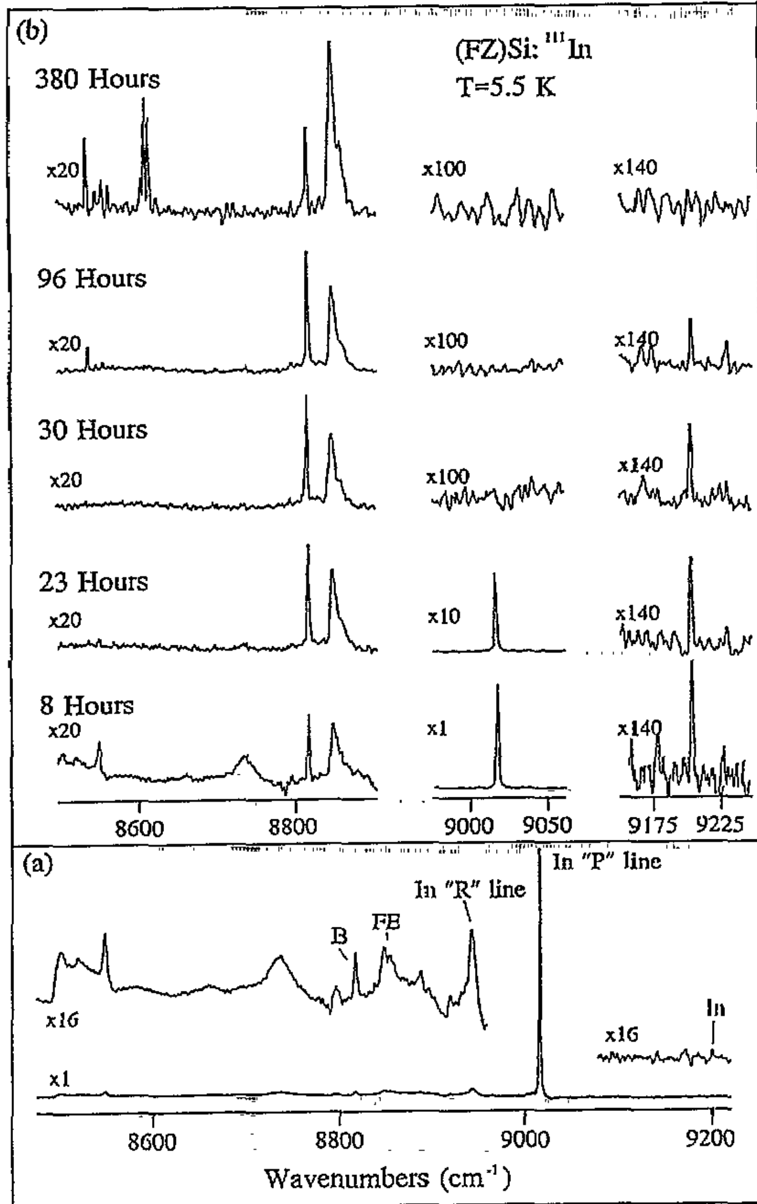

Figure 2. (a) PL spectrum of quenched Si:^{111}In recorded at 5.5 K. The main features in the spectrum are labelled as explained in the text. (b) PL spectra of quenched Si:^{111}In recorded at 5.5 K over a period of 16 days. Gain changes are indicated in the figure. For the spectrum recorded after 380 hours, the sample temperature is slightly higher than the nominal 5.5 K. This accounts for the apparently weaker boron phonon-assisted bound exciton recombination in this spectrum. This spectrum also suffers from somewhat greater noise which we attribute to spurious contributions to the original interferogram.

The Si:^{111}In sample was first annealed three days after implantation. Intense PQR luminescence was observed with a P line signal to noise ratio of ~800. Within 1 d the signal was no longer detectable—an extraordinary result when a 2.8 d half-life was expected. The sample was annealed again, this time six days after implantation. The PQR luminescence signal was recovered to approximately the same signal level. The rapid loss of intensity was confirmed and the data which reveal this are shown in figure 2. The full spectrum shown in figure 2(a) was recorded approximately two hours after quenching. The main line P and its associated sidebands dominate the spectrum, extending to the O^{Γ} cut-off at ~8940 cm^{-1}. Both free exciton (FE) and boron bound exciton (B) lines can also be observed. The neutral indium acceptor BE line, however, is barely detectable. Increasing the laser power from 100 mW to 140 mW caused an increase of only 4% in the P line intensity without producing any In acceptor BE PL.

The lowest spectrum in figure 2(b) is that for eight hours after quenching. Here the P line intensity is lower by a factor of ~2 and the In acceptor BE line is now evident. The evolution of the spectrum is shown in the remaining spectra of figure 2(b). Both the PQR spectrum and the neutral In acceptor BE line decrease in intensity, the former very rapidly, while the FE and B lines maintain their intensities very well. New lines which appear after long delays are discussed below.

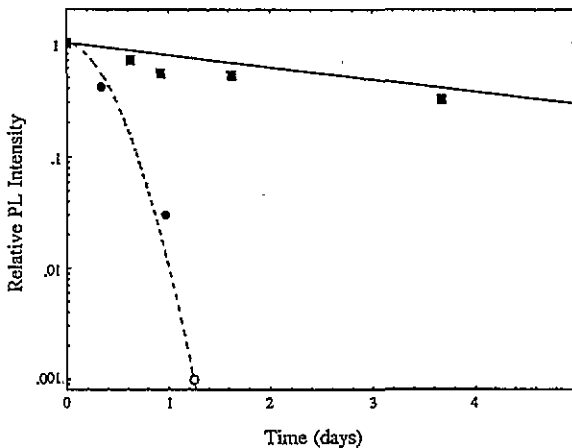

Figure 3. The changes in the intensity of the In-related features in the PL spectra of Si:^{111}In. The solid line shows the changes expected for a 2.8 d half-life. The squares and circles are data points for the neutral In acceptor bound exciton and the PQR centre, respectively. The final datum point for the PQR centre corresponds to the noise floor—the line was not detectable at this time. The broken line curve is explained in the text.

The main results are illustrated in figure 3 which shows the intensity decrease of both the P line and the In acceptor BE line with time. For the neutral In acceptor BE line we used the spectrum after eight hours as origin. The solid line in figure 3 shows the change expected for a 2.8 d half-life. The acceptor bound exciton intensity is seen to follow this closely, whereas the PQR intensity departs markedly. The most likely explanation for the latter is the passivation of the PQR centres. It is known that the PQR PL intensity slowly degrades with time following a quench for bulk In-doped samples [8]. However, we find that samples implanted with stable ^{115}In and similarly annealed do not display the marked

behaviour of ^{111}In. Several possibilities should be considered as the passivating species. Since the concentration and total population of PQR centres are both very low, trace amounts of impurities which are mobile at room temperature could readily lead to total passivation. Transition metal contamination is one likely source of the passivation. We must also consider the presence in the implanted layer of ^{111}Cd daughter atoms produced in the decay of ^{111}In. The diffusivity of Cd in Si at room temperature is not known. However, given the proximity of the implanted ions—the straggle is only 13 nm—even a small value could be sufficient to cause daughter ^{111}Cd atoms to migrate to surviving In PQR centres. In this scenario, the decrease in the P line intensity can be modelled by the following expression

$$I(t) \propto \exp(-\alpha t)\exp(-\beta(1-\exp(-\alpha t))t)$$

where $\alpha = 0.247$ d^{-1} is the radioactive decay probability, β (an adjustable parameter) is a measure of the probability of capture by surviving ^{111}In PQR centres of daughter ^{111}Cd atoms for which the concentration as a function of time is proportional to the factor $\{1-\exp(-\alpha t)\}$. This simple formula neglects any source of passivation other than the decay of ^{111}In atoms, but it does produce qualitatively the observed time dependence of the PQR intensity. The broken line of figure 3 is obtained for $\beta = 20$ m^3 d^{-1}.

The second striking result of the experiment is the emergence of new lines in the PL spectrum which begin to appear approximately one ^{111}In half-life after quenching (figure 2). We can clearly identify three groups of lines, the first to appear being near 8550 cm^{-1} and another, which appears clearly only after more than ten days, being centred near 8610 cm^{-1}. To our knowledge, these spectra have not been reported previously. A complex line structure and temperature dependence is observed as shown in figure 4. The signal levels, though adequate to clearly reveal the line structure, are too poor to enable accurate thermalization data to be produced. Similarly, insufficient data exist to fit the growth in the intensity of the new spectra to the decay of ^{111}In atoms. The third group of lines is evident in the data of figure 4. The lines fall in the range 8680–8780 cm^{-1} and they appear only at temperatures from ~10 K upwards. Although these lines appear at first sight to involve excited states of the 8550 cm^{-1} group, it is clear from the data for the sample 380 hours after the quench that the relative intensities are not constant. We must conclude that different defects are involved; the unusual temperature dependence of the PL will be addressed in the future.

It is noteworthy that the intensity of the luminescence for all new spectra is of the same order of magnitude as the boron acceptor bound exciton emission, and certainly much less than that observed for the PQR isoelectronic centre. It is likely, therefore, that the centres producing the new spectra are donor or acceptor in nature rather than isoelectronic. Substitutional Cd would be expected to produce double-acceptor bound exciton recombination which has never been observed in silicon although examples exist for Ge [11–13]. The complexity of the line structures we observe may well be consistent with such recombination, but such a conclusion is tentative. The PL intensities are too weak to reveal either two-hole or two-electron satellites which would confirm the nature of the recombination centres. A variety of samples with greater initial doses of ^{111}In will be studied to explore this subject further.

Finally, the influence of the radioactive decay process must be considered. The capture of an inner shell electron by the parent ^{111}In nucleus leads to substantial energy release by the ^{111}Cd daughter, culminating in the production of two γ-rays per disintegration. Although much of this energy is deposited in the crystal there is no evidence from many experiments using ^{111}In in PAC [14] that defect production adjacent to the In/Cd atoms is significant. Furthermore, the total radiation dose received by the crystal from a typical implant dose

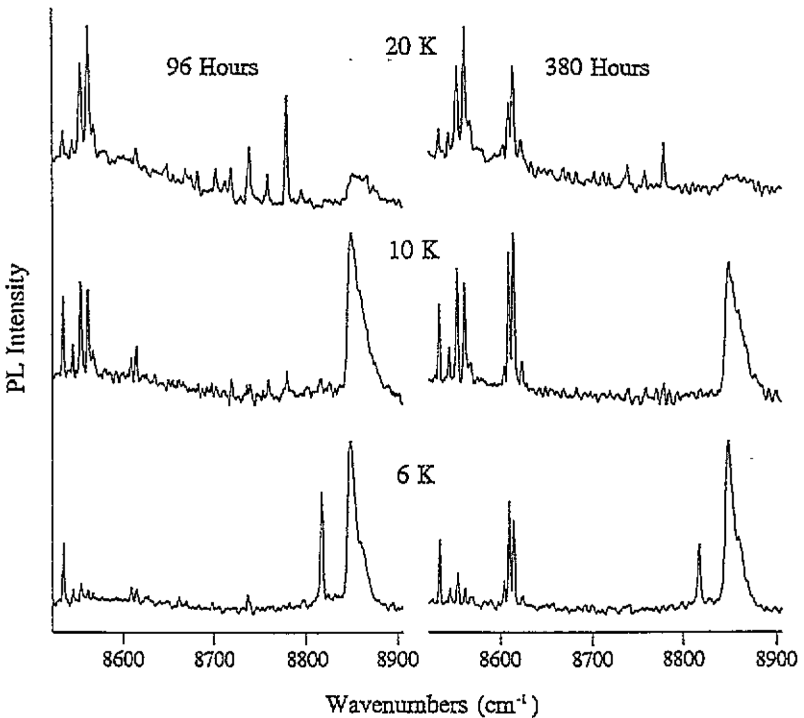

Figure 4. The temperature dependence of the new PL spectra observed in Si:^{111}In following the decay of ^{111}In to ^{111}Cd.

of 10^{11} atoms is orders of magnitude less than the norm for PL defect production [15]. Accordingly, the effects of the decay process itself can be neglected.

In conclusion, we report the results of a photoluminescence study of Si implanted with the radioactive isotope ^{111}In. Dramatic changes are observed in the intensity of the isoelectronic bound exciton recombination spectrum 'PQR' which are too fast to be attributed to radioactive decay alone. Complexing of the daughter Cd atoms or other trace impurities with surviving centres is proposed to account for the rapid loss of signal. The substitutional In acceptor bound exciton is found to decay at a rate appropriate for the ^{111}In half-life. Several groups of new lines appear in the spectrum also over periods of days and weeks. A complex temperature dependence is observed for these spectra and available data indicate that they originate in donor or acceptor, rather than isoelectronic, centres. The evolution of these centres is believed to be due, at least in part, to the slow diffusion and complexing of the ^{111}Cd daughter atoms in the crystal when stored at room temperature. The results establish the feasibility of using radioactive isotopes in PL spectroscopy and they also provide a striking illustration of how such experiments may be exploited in the study of defects in all classes of semiconductor. Despite the success of this experiment, however, practical considerations invoke some cautionary remarks. Firstly, the production of suitable isotopes in sufficient quantities and with adequate mass separation must be achieved. Yields must be high in order to implant the necessary dose in a reasonable time. Half-life values also impose severe constraints; values of the order of hours require both high yields and on-line PL facilities, while values of the order of

several weeks or longer are not well suited to PL spectroscopy because of the difficulties associated with quantitative PL measurements. Nevertheless, there are many problems in the characterization of semiconductors, particularly regarding the chemical identification of impurity centres, which should be amenable to PL analysis using this approach. Other high-sensitivity techniques such as EPR and PTIS should also prove to be particularly suitable for use in conjunction with radioactive isotopes.

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