Electrically Detected Magnetic Resonance Applied to the Study of Near Surface Electron Donors in Silicon

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Electrically detected magnetic resonance (EDMR) is applied to devices with implanted leads and a 50 μm square gap laid down on bulk phosphorus doped silicon. Devices with a range of phosphorus concentrations and surface types were prepared and measured to examine the interplay between donor and charge trap states in producing EDMR signals.

1. Introduction

Magnetic resonance of donors in semiconductors via electron spin resonance (ESR) is well established. In particular the ESR of shallow electron donors in silicon was first achieved in the 1950's [1]. However, the sensitivity of conventional ESR is limited, requiring samples with 10^{10} donors or more. This problem can be overcome by detecting magnetic resonance via the effects of spin selection rules on other observables, such as charge transport.

Electrically detected magnetic resonance (EDMR) is where a change of the dc conductivity due to spin resonance is observed. EDMR was first demonstrated on Si:P by Schmidt and Solomon [2]. More recently, McCamey *et al.* [3] showed that EDMR could be used to detect as few as 50 spins in a submicron size silicon device into which the phosphorus donors had been implanted. EDMR is also particularly useful in the study of surface defects on semiconductors and their influence on donors placed near to the surface. In the case of shallow donors (eg phosphorus) in silicon (Si:P), it has been proposed that the spin dependent recombination/scattering of the photoelectrons proceeds via a process also involving (deeper energy) surface electron traps like the so called P_b silicon interface dangling bonds [4].

In this paper we describe the development of a robust multi-micron EDMR device in silicon, with a view to detailed comparisons of the effects of different surface preparations, as well as variations in donor profiles. Preliminary results using bulk doped substrates with native and thermal oxides, as well as H- and D-terminated surfaces are presented and discussed.

2. Experimental details

A series of bulk doped, Si:^{31}P EDMR devices with various surface terminations were prepared using optical photolithography techniques. Three doping densities, 3×10^{15}, 2×10^{16} and 1×10^{17} P cm^{-3} were used together with the following four different surface types (i) native oxide, (ii) high quality thermal oxide, (iii) H- and (iv) D-terminations (SiH & SiD). An electron microscope image of a typical device is shown in Fig. 1. The gap between the leads is 50 μm square and the buried metallic (highly doped) leads were created via low energy ion implantation of P^+. An RTA anneal was applied post implantation of the leads to repair damage. Large evaporated Al ohmic contacts allow direct coupling of current leads without the need for wire bonding to external contacts. The device design minimises the number of process steps and allows the metal contacts and external leads to be kept away from the microwave active region in the ESR cavity. All surfaces were prepared prior to implantation and annealing by cleaning (piranha and RCA2) with a subsequent removal of the pre-existing native oxide using hydrofluoric acid (HF). Controlled 5 nm thick thermal oxides were grown at 820°C. The H (D) terminated surfaces were prepared by etching the native oxide after processing with a 5% HF in H_2O (D_2O) reagent. These later surfaces were preserved by a final covering with photoresist.

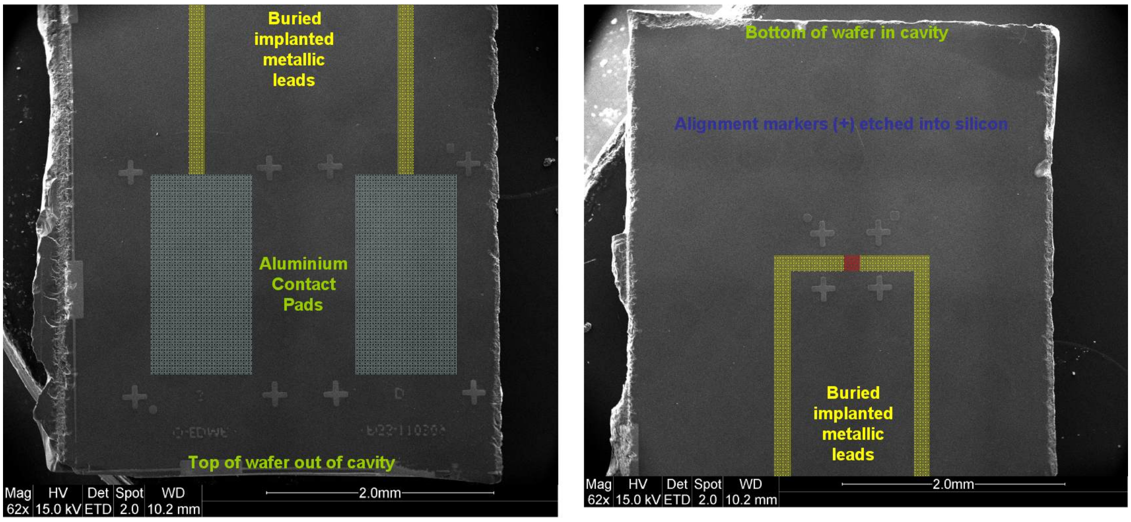

Fig. 1. Scanning electron microscope images of the upper and lower halves of an EDMR device.

The EDMR apparatus at the Walter Schottky Institute utilises a standard x-band ESR system to provide the microwaves, dc and modulated magnetic fields. The measurements presented here were carried out at approximately 5 K and a steady photo current of a few μA was facilitated by a dc voltage from a battery source and white light from a halogen lamp. A lock-in amplifier provided the modulation signal at 1.23 kHz, and was also used to detect the EDMR signal from the device current.

The character of the EDMR spectra expected from Si:P are as for conventional ESR. An isolated donor electron, with S = 1/2 coupled to I = 1 /2 ^{31}P nucleus, results in a hyperfine split doublet centred at g = 1.9987 (~3473 G in the spectra below) with ~42 G splitting [1]. If donor pairs or clusters are present (exchange coupled), a central line may also exist [5]. Charge traps also result in ESR lines. In particular an electron at an interface dangling bond (P_b centre) is commonly observed (two overlapping broad lines at g ~ 2.004 and 2.008 for the magnetic field B_0 parallel [110], often appearing as a single very broad line at g = 2.0055).

3. Results

EDMR spectra collected for the three P concentrations and the various surface types are illustrated in Figs 2a, b and c. In all cases the maximum P and P_b signals occur with the thermal oxide surface. This is perhaps unexpected given that the thermal oxide should have a much lower P_b trap areal density than the native oxide. The results for the thermal oxide cases are reproduced for direct comparison in Fig 2d. Surprisingly there is little variation in the signals as a function of P concentration, over nearly 3 orders of magnitude, and indeed are slightly smaller at the higher concentration (10^{17} cm^{-3}).

Integrated signal strengths are estimated for comparison and summarised in Table 1. The trend is clear with the P and P_b signal magnitudes moving in concert. The devices with thermal oxide surfaces have the largest signals, while native oxides have the smallest (of the pre-prepared set). These trends are virtually independent of the P concentration. The H- and

D-terminated surfaces provide signals intermediate between the other two. These preparations, however, do not appear to represent true trap free interfaces when compared to the results in Fig 3, where much smaller signals were obtained from a freshly prepared (i.e. just prior to measurement) SiH surface.

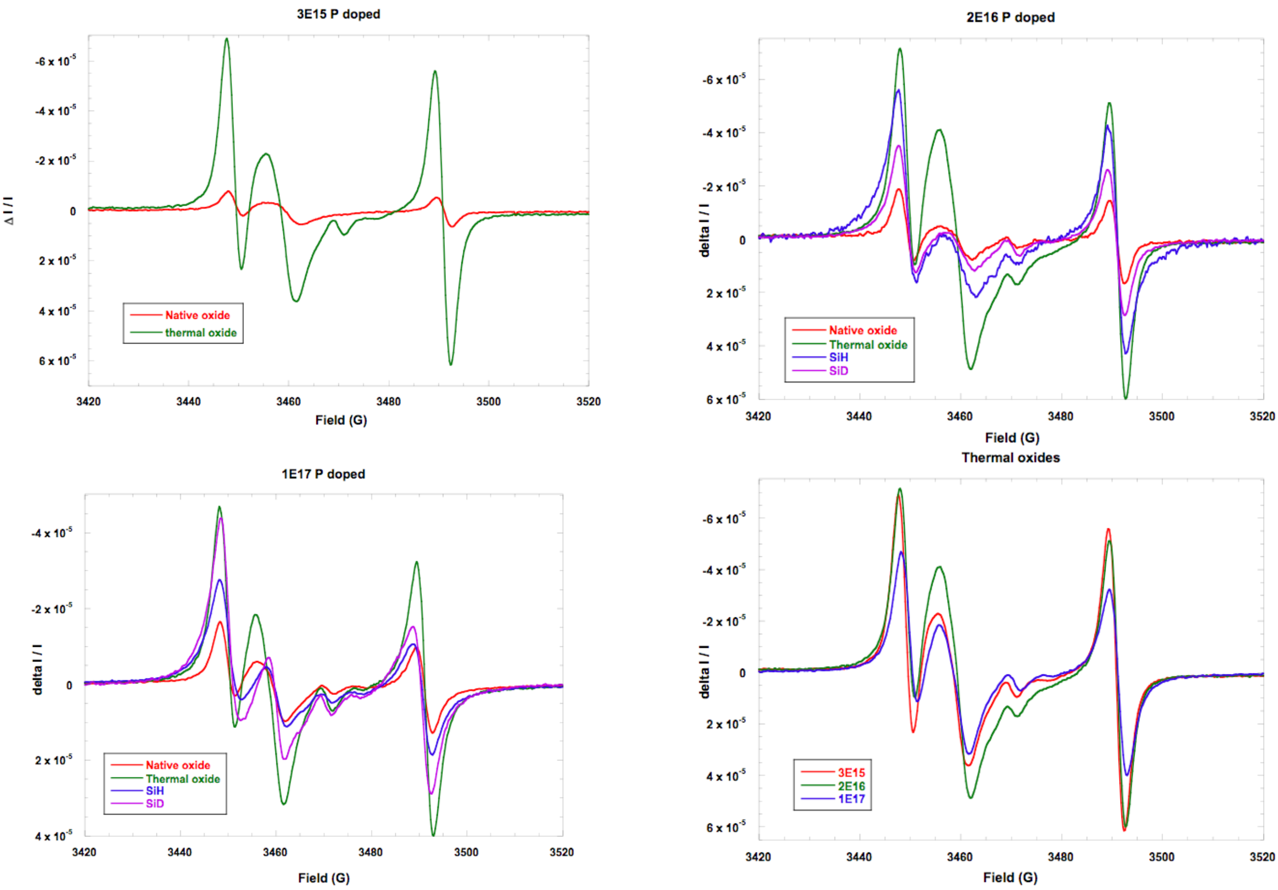

Fig. 2. (a), (b) and (c) are EDMR signals collected at ~5 K for Si:P devices with 3 x 10^{15}, 2 x 10^{16} and 1 x 10^{17} P cm^{-3} respectively, for various surface types as labelled. The data in (d) are the thermal oxide results repeated for direct comparison.

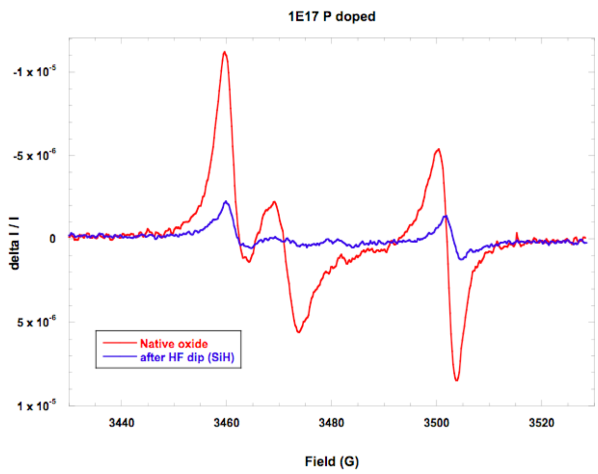

Fig. 3. EDMR signals collected at ~5 K for Si:P device with 1 x 10^{17} P cm^{-3}, with native oxide surface and immediately following a HF etch which replaced the oxide with a hydrogen terminated surface.

Table 1. Parameters from least squares fits to the spectra.

sample	sample parameters (concentrations in cm-3)	Signal (Arb. Units)		
		Pb	P doublet (total)	Centre
J1	1E17 doped native oxide	1374	750	76
N3	1E17 doped thermal oxide	4366	3052	152
J9	1E17 doped SiH	1294	1390	87
A12	1E17 doped SiD	2345	2166	141
D3	2E16 doped native oxide	644	652	55
V4	2E16 doped thermal oxide	5905	3802	44
D4	2E16 doped SiH	1140	3536	44
D11	2E16 doped SiD	712	1842	57
L4	3E15 doped native oxide	427	378	0
Y3	3E15 doped thermal oxide	3084	3858	53
J10	1E17 doped native oxide	351	314	8
J10	1E17 doped SiH (fresh)	24	58	3

4. Discussion

These results clearly demonstrate that a photocurrent recombination model for EDMR in Si:P requiring the presence of deep charge traps is valid. There is an optimal relative concentration of traps to donors to get large EDMR resonances. Too many traps (eg native oxide) deplete donors. With too few traps (fresh SiH) the recombination path is blocked (NB our large area pre-prepared SiH and SiD were likely degraded between preparation and measurement c.f. the freshly dipped case). Anecdotally, from our measurements the thermal oxides in combination with bulk P densities between 10^{15} to 10^{16} cm^{-3} seems optimal for maximum strength EDMR signals. Good thermal oxides on Si typically have an interface trap density of ~10^{11} cm^{-2} eV^{-1} [6] which corresponds to an average spacing of about 3 x 10^{-6} cm. While 3 x 10^{15} and 2 x 10^{16} P cm^{-3} have average donor spacings of 7 x 10^{-6} cm and 3 x 10^{-6} cm respectively.

One other puzzle is the lack of variation in the P central line. Paired and clustered donors should be present in reasonable numbers only at higher (1x10^{17} cm^{-3}) P concentrations. It could be that some of this small signal is associated with regions of straggle near the implanted leads.

Acknowledgments

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