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Lawrence Berkeley Laboratory[1] and University of California

Grain Boundaries in Germanium: Effects of Exposure to Plasmas

By
K.S. JONES and S.J. PEARTON

A number of recent investigations have dealt with the neutralization of grain boundary electrical activity in Si /1 to 3/ and GaAs /4/. The most effective treatment has proved to be exposure of the polycrystalline material to a low pressure hydrogen plasma. Enhanced diffusion of the atomic hydrogen along the grain boundaries enables penetration depths of several mm in polycrystalline Si /2/, and there is clear evidence of reductions in defect state densities and potential barriers associated with the grain boundaries after hydrogenation. The incorporation of Li into Si grain boundaries has also been shown to passivate the electrical effects of these line defects /5/, but Li is a shallow donor impurity in Si, and thus may produce unwanted modifications of the bulk properties of the semiconductor. In this note, we investigate the effects of plasma exposure on the electrical activity of grain boundaries in high purity n- and p-type Ge. The effects of gas ion or atom incorporation in the grain boundary containing material is measured by the effect on reverse bias diode leakage current and capacitance. This investigation has been prompted by potential application to Ge devices, such as large volume nuclear radiation detectors /6/, and the desire to measure such effects in a high purity material in which impurity precipitation on dislocations within the grain boundaries is minimized.

Samples were cut close to the "last-to-freeze" end of Ge crystals grown from synthetic silica crucibles under a hydrogen atmosphere. Conductivity measurements at 77 K revealed net impurity contents of $\approx 10^{11}$ cm^{-3} for both n- and p-type material. The grain boundaries were delineated by etching the lapped surfaces of the samples in a mixture of 4 HNO_3: 1 HF. Implantation of 25 keV ^{11}B or ^{31}P to opposite faces of the slices (dose 10^{14} cm^{-2}) followed by an appropriate annealing cycle formed degenerately doped p^+ and n^+ contacts, respectively. The slices were cut into 5x5x1.5 mm^3 samples, the contacts masked and the sides etched to produce a specular finish. Current- and ca-

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[1] 70 A/3363, 1 Cyclotron Road, Berkeley, California 94720, USA.

pacitance-voltage characteristics before and after plasma treatments were recorded at 77 K using an electrometer and a 1 MHz capacitance bridge. Exposure to the atomic species of the various gases were performed in the system described previously /7/. High purity gases were used for all experiments, and a water vapor plasma was produced by gradual evacuation of an enclosed source of water contained within the plasma system. Molecular gas anneals were performed in the same apparatus, without application of the radio-frequency power to ionize the gas.

Fig. 1 shows typical I-U characteristics of the p-type samples prior to plasma treatment. Because of the presence of grain boundaries in the material these leakage currents are approximately three orders of magnitude higher than expected for single crystal material of the same net impurity content. Heating the polycrystalline samples at 400 °C for 3 h in plasmas of N, Ar, O, or water vapor generally increased the reverse leakage current by approximately a factor of two. This may be related to an increase in the defect state density associated with the grain boundaries due to the outdiffusion or recombination of hydrogen already present in the crystal from crystal growth, or the incorporation of the various gas atoms. The water vapor plasma will contain ionized and neutral hydrogen and oxygen as well as the species OH. In some samples we saw a slight improvement in diode characteristics after water vapor plasma exposure, due most likely to the effects of the atomic hydrogen present in the plasma overwhelming the negative effects of the oxygen. The OH species is a shallow donor impurity in quenched Ge /6/, and might be expected to pair with acceptor-like states within the grain boundaries producing a neutralization effect, in analogy with Li. However, we saw no consistent evidence for such an effect in

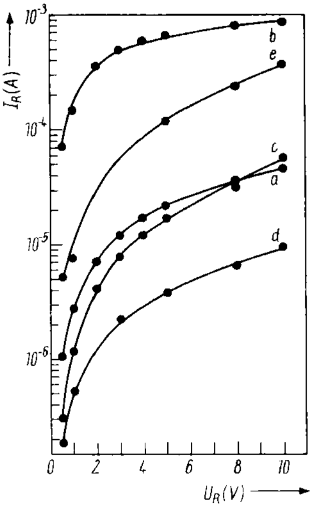

Fig. 1. Current-voltage characteristics of p-type polycrystalline Ge diodes: (a) as fabricated, (b) after heating in molecular hydrogen for 3 h at 400 °C, (c), (d) heating in atomic hydrogen for 3 h at 300 and 400 °C, respectively, and (e) heating in atomic hydrogen for 3 h at 400 °C and subsequent vacuum annealing for 3 h at 500 °C; $N_A - N_D \approx 10^{11}$ cm^{-3}

our samples. Heating the samples for the same conditions in the molecular species of the different gases produced similar degrees of leakage current deterioration.

As fluorine has been shown to increase the potential barrier heights of grain boundaries in Si /8/, we attempted to incorporate fluorine into Ge by exposure of the sample to an SF_6 plasma, but the severe plasma etching associated with this species prevented a determination of its modifying action on the Ge grain boundaries.

The only atomic gas species which proved consistently effective in reducing the reverse leakage currents of the polycrystalline Ge diodes was hydrogen.[2] Fig. 1 also shows the lowering of the diode leakage current of the p-type material after a 3 h exposure to a hydrogen plasma at 400 ^oC. The amount of this improvement was in general related to the amount of lineage in a particular sample, but even for samples with seemingly comparable degrees of crystallinity there were variations in the improvement observed. This indicates that the microscopic nature of the grain boundaries is important in determining both the leakage current and the effectiveness of hydrogen passivation. Quantitatively similar results were obtained on the polycrystalline n-type Ge. Such behavior has also been observed for hydrogen incorporation in polycrystalline Si /2/. We checked that the plasma induced changes in the diode characteristics were not simply a surface passivation effect by fabricating guard-ring structures and thus eliminating the surface component of the diode leakage current. The lowered leakage currents were seen only in hydrogenated samples. As well, single crystal samples treated in the hydrogen plasma usually displayed slightly higher (typically a factor of 2) reverse leakage currents after the plasma treatment.

We performed the hydrogenation treatments of the polycrystalline Ge at various temperatures (300, 400, 500 ^oC) for 3 h on both the n- and p-type material. Saturation of the lowering of the diode reverse leakage current was obtained by plasma exposure at 400 ^oC. For 500 ^oC exposures we saw slightly less improvement than for plasma exposure at 400 ^oC even though the solubility of hydrogen is higher at 500 ^oC indicating that outdiffusion of the hydrogen incorporated from the plasma becomes significant at the higher temperature.

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2) A similar result was observed by /9/.

This was more obvious after performing vacuum anneals under the same conditions on plasma treated samples in which we observed increases leakage currents due to hydrogen outdiffusion from the grain boundaries. This effect was most evident at 500 °C, where the I-U characteristics were returned to their original values.

Comparing the leakage current characteristics before and after hydrogenation one may estimate the hydrogen incorporation depth by determining the reverse bias to which lowering of the leakage current is observed. Using the approximation /10/

$$d = 5.4\sqrt{Dt}\,,$$

where d is the diffusion depth of the hydrogen in time t at a temperature at which the diffusion coefficient is D, we calculate that at 300 °C, $D_H = 1.3\times 10^{-9}$ cm^{2}s^{-1}, and at 500 °C, $D_H = 2.9\times 10^{-9}$ cm^{2}s^{-1}. Extrapolating results from high temperature outdiffusion experiments /11/, we obtain diffusivities of 1.2×10^{-6} and 9×10^{-6} cm^{2}s^{-1}, respectively, at 300 and 500 °C. It is known that in bulk Ge the diffusivity of hydrogen is lowered by approximatively four orders of magnitude by defect- and self-trapping mechanisms at these temperatures /12/. The comparison of the results in polycrystalline material with the extrapolations of the high temperature bulk diffusion data (obtained under conditions of unimpeded hydrogen diffusion) show that at temperatures of 300 to 500 °C the diffusion of hydrogen in polycrystalline Ge is approximately an order of magnitude faster than in bulk Ge. Such an enhanced diffusivity of atomic hydrogen in the presence of grain boundaries is not unexpected /13/.

Fig. 2 shows C-U data from the p-type polycrystalline samples before and after hydrogenation. The plasma treatment at 400 °C modifies the characteristic to resemble more closely that of an ideal diode of this net impurity content. However, we note that even after this optimized hydrogenation the polycrystalline sample is still far from ideal. This is emphasized by the I-U characteristics of Fig. 1, which even after hydrogenation of the sample are approximately two orders of magnitude higher than those of single crystal samples of the same net impurity content.

In conclusion, we have demonstrated that hydrogen is effective in passivating the electrical activity of grain boundaries in Ge, and that there is an enhanced diffusivity of the atomic species along these boundaries. However,

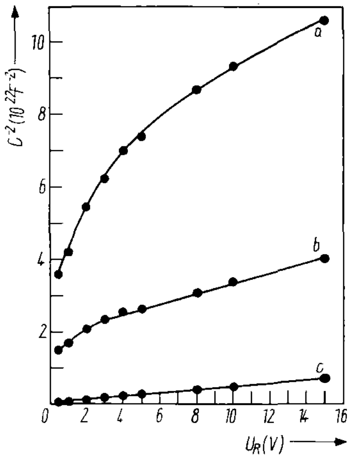

Fig. 2. Capacitance-voltage data for p-type polycrystalline Ge diodes: (a) as fabricated, (b) after heating for 3 h at 400 °C in a hydrogen plasma, (c) ideal diode of the same doping density and dimensions; $N_A-N_D \approx 10^{11}$ cm^{-3}

even under optimized hydrogenation conditions the diode characteristics of plasma treated polycrystalline samples are inferior to those of comparable single crystal samples.

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