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Hydrogen implantation defects in MgO

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Abstract

Deuterium and hydrogen ions with an energy of 15 keV have been implanted in virgin MgO (1 0 0) single crystals and in single crystals containing helium implantation generated microcavities. Doses were varied from 2×10^{15} to 2×10^{16} cm^{-2}. The samples were annealed from room temperature to 950 K. The defects produced by hydrogen and the trapping of hydrogen at the defects were monitored by photon absorption and positron beam analysis. With this novel technique a depth distribution of defects can be determined for implantation depths from 0 to 2000 nm. The technique is very sensitive for vacancy and vacancy clusters, i.e. sites with low electron density. After 950 K annealing microcavities were observed for the 2×10^{16} cm^{-2} dose but not for the 10 times lower dose. During annealing up to 750 K point defects are mobile but the defect clusters remain small and filled with hydrogen. In samples which contain already microcavities, point defects and deuterium from the deuterium irradiation are accumulated by the microcavities.

Keywords: Positron; Ion implantation; Hydrogen; Deuterium; Oxide

1. Introduction

The observation of optically active metallic nano-precipitates in ion implanted ceramics [1] has given a considerable impetus to the study of nucleation and growth of these precipitates. In the past the formation of high temperature stable nano-size noble gas precipitates or bubbles have been reported for MgO [2] and UO_2 [3]. In a study of helium implanted MgO we showed that helium bubbles were formed after annealing to 750 K and that to our surprise helium was released from the bubble cavities during thermal annealing at 1300 K [4,5]. In the present article we discuss results we obtained for deuterium irradiated MgO irradiated and annealed under similar conditions as in the helium work.

2. Experimental

The samples were 1 mm thick cleaved MgO (1 0 0) crystals purchased from Kelpin GmbH (Hamburg, Germany) and Mateck GmbH

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(Juelich, Germany). Implantation was performed at room temperature. The current density was about 3 μA cm^{-2} of D_2^+ ions of 30 keV energy. The beam was uniformly sweeped over the implantation area by using deflection plates. Implantation of molecule ions at this energy causes no problems regarding channeling of the implanted particles, because the molecule ions break up and are implanted individually in an off-channel direction. Thermal annealing was performed in a tube oven in ambient air for periods of 30 min. All samples were before and after the implantation, and after annealing steps checked on the presence of optically active defects by absorption spectroscopy in the visible light (Hewlett Packard 8452A spectrometer). Positron beam analysis [6] was performed to measure defect depth profiles and establish the nature of the defects. Positrons have a high affinity to be trapped at sites with reduced atomic density like in vacancies and at precipitate–matrix interfaces. The character of the defects is related to deviations of the electron-momentum distribution observed as Doppler Broadening of the 511 keV annihilation gamma peak. The shape of the profile is characterised quantitatively with the aid of two parameters: S and W. The parameter S gives the area under the central part of the profile, divided by the total area under the profile; thus a high value of S signals the presence of open-volume defects, whereas a 'defect-free' sample will show a low value of the S parameter. The energy windows are set symmetrically around the centre of the peak in such a way as to maximize the sensitivity to vacancies. An S value of $\sim$0.50 for defect-free metals is usual. The second parameter, W, gives the ratio between the area under the wings and the total area and is sensitive to annihilations with core electrons of the atoms in the material. For defect-free MgO in this work $S = 0.48$ and $W = 0.075$. An important property of S and W is their linearity. By this we mean that if there are several possible modes of positron annihilation in a material with probabilities f_i and corresponding S parameters S_i, then the measured S parameter will be found from $S = \sum_i f_i S_i / \sum_i f_i$ with a corresponding expression for W. One can make use of this by plotting S and W in a graph of S against W in an S–W map [7]. The running parameter in this work is the positron energy or positron implantation depth. When only two states are present the points will be on a straight line connecting the two states. In general the positron energy dependent fractions can be predicted or fitted by a program that solves the positron diffusion and trapping equations for positrons implanted in layered systems [6]. Depth information on defects is obtained via the known implantion profile of the positrons. The mean implantation depth for MgO is $\langle z \rangle = 10\ E$ [in keV]$^{1.62}$ nm, with E the positron implantation energy.

3. Deuterium implantation and annealing

Fig. 1 shows the S vs. E curves for the highest and lowest deuterium dose of this work. For two cases the S–W map is shown: for the as irradiated and 950 K annealing of the highest dose. The following remarks can be made.

1. *The depth below the surface of the defects.* The defects in the as irradiated samples are observed at larger mean depth 230 nm, than in the high dose annealed sample (>550 K), 130 nm. The first depth is beyond the implantation depth of the deuterium calculated by TRIM [8]. The defects might be ascribed to a low concentration of defects created by diffusing interstitials or dechanneled–channeled projectiles. Because of the high sensitivity of positron analysis (better than 1 appm neutral defects) the defects will be noticed. This tail-effect is commonly observed in positron beam analysis [9]. Apparently the defects at the implantation depth of the deuterium are not well observed. It has been shown that hydrogen decorated defects in silicon have a strongly reduced S-parameter. Therefore, we ascribe the effect to the presence of vacancies saturated by hydrogen.

2. *Photon absorption* indicates the presence of F-centres (V_O). From the measured attenuation coefficient for the 2×10^{15} cm^{-2} D^+ irradiated sample an areal F centre concentration $<5\times10^{13}$ cm^{-2} is calculated if an absorption cross-section $\sigma_{abs} > 10^{-15}$ cm^2 is assumed. TRIM results yield 0.05 vacancy (V_{Mg} and V_O together) per D^+-ion of 15 keV without taking recombination into

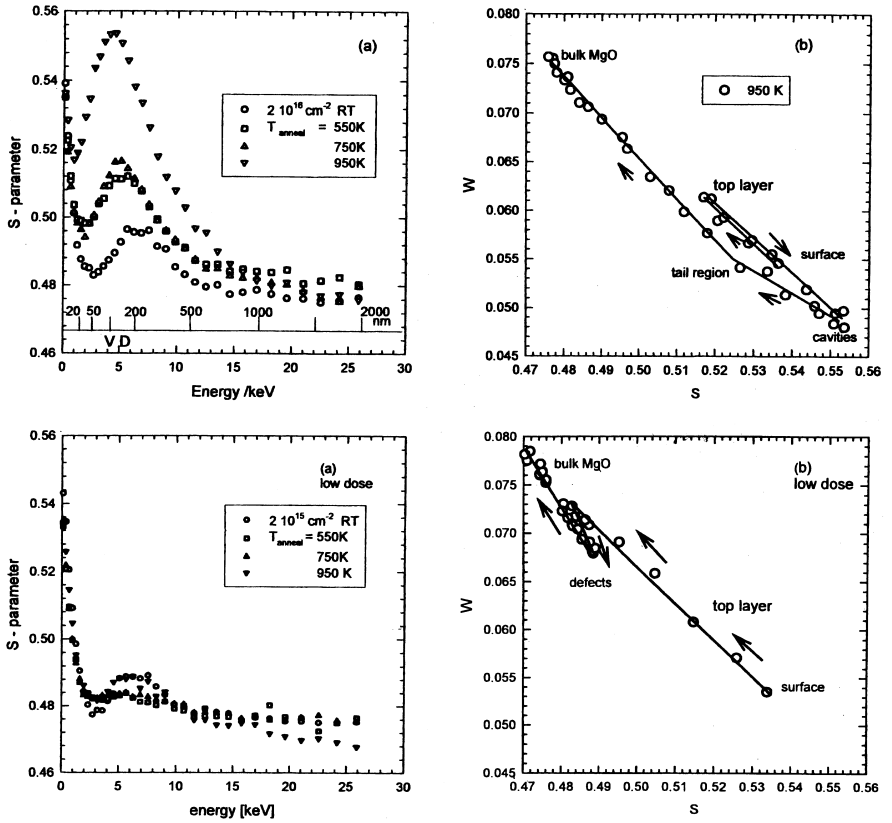

Fig. 1. (a) The *S*-parameter plotted vs. positron implantation energy for high and low dose deuterium implanted MgO (1 0 0) crystals in the as irradiated state and after annealing to 550, 750, and 950 K, respectively. A depth scale is plotted with the positions of the maximum defect density (V) and maximum density of implanted deuterium (D) indicated. (b) *S*–*W* maps for the high and low dose sample after annealing to 950 K.

account; thus 10^{14} cm^{-2} vacancies, which is of the right order of magnitude.

3. *Cavities*. During *thermal annealing* of the high dose sample deuterium and vacancies will meet and form small deuterium vacancy complexes. The vacancy distribution is centered around 130 nm (TRIM) and therefore the vacancy complexes are formed here. The value of the *S*-parameter is about 7% higher than the bulk value for MgO which is considerably higher than expected for monovacancies. At a temperature of 550 K most F-centres have disappeared which is another proof for clustering. It is likely that some deuterium has left this zone, else the *S*-value should have been lower. Hakvoort et al. decorated cavities in silicon with hydrogen and observed a considerable reducing effect on *S* [10]. In the temperature range from 750 to 950 K further growth takes place which leads to an *S*-value of 18% higher than bulk MgO. This means that cavities are sufficiently large, i.e. >1 nm, to accommodate positronium (e^+–e^-). It can be shown that the theoretical *S*-value for positronium amounts to 0.577 is 22% higher than MgO [5]. Thus cavity concentration has grown so high in the top layer that nearly all positrons are trapped as positronium in cavities. Presumably all deuterium has left the layer.

4. *Threshold for cavity formation*. The low dose experiment reveals a reduction of *S* during annealing from 550 to 750 K, which might point to loss of vacancies and decoration by deuterium of

the remaining vacancies. After 950 K annealing there is a slight increase of S indicating that some cavities have been formed. They are formed at larger depth than the average depth of the vacancies because cluster probability increases with depth for low vacancy concentrations.

4. Deuterium post-irradiation of pre-existing cavities

In order to see effects of pre-existing traps we used a MgO sample that was irradiated with 30 keV ^{3}He ions at a dose of 8×10^{15} cm^{-2}. After annealing to 1300 K it was established that the sample contained microcavities [5]. This sample was used to decorate the cavities by irradiation with 4×10^{15} cm^{-2} 15 keV D^+ ions at room temperature. A second sample without cavities was implanted with the same deuterium probe dose to act as reference during thermal annealing of both samples. The annealing behaviour is shown in Fig. 2. The following comments can be made.

1. *Depth distribution of the defects.* After the room temperature deuterium irradiation the S parameter in the zone of the cavities has been reduced. Apparently the deuterium vacancies formed in the cavity zone competed with the cavities in trapping positrons giving rise to a lower S. In fact the result can be described as a superposition of the new defects on the existing defect distribution.

2. *Thermal annealing.* A similar description can be given for the annealing from 550 to 750 K. The increase of S in the reference sample matches nearly the increase of S in the zone where the cavities are found in the cavity sample. Thus at these temperatures there is only short range transport. However, annealing at 950 K gives a different picture. In the reference sample a broad distribution of vacancy complexes extending to large depth develops. But in the cavity sample the cavity distribution remains located at the position of the pre-existing cavities. Thus, the cavity zone acts as a strong trap for vacancies that are released when smaller vacancy clusters at 950 K have been dissociated.

5. Vacancy clustering and the role of deuterium

There is not yet direct evidence from our experiments on the temperatures where interstitial deuterium becomes mobile and is released from vacancies. Preliminary thermal desorption experiments on 150 eV deuterium irradiated MgO surfaces indicate several contributions to the D_2 desorption spectrum in the temperature range from 450 to 950 K. A dominant contribution was at 650 K. Taking into account the higher heating rate (3 K/s) and the shallow implantation depth

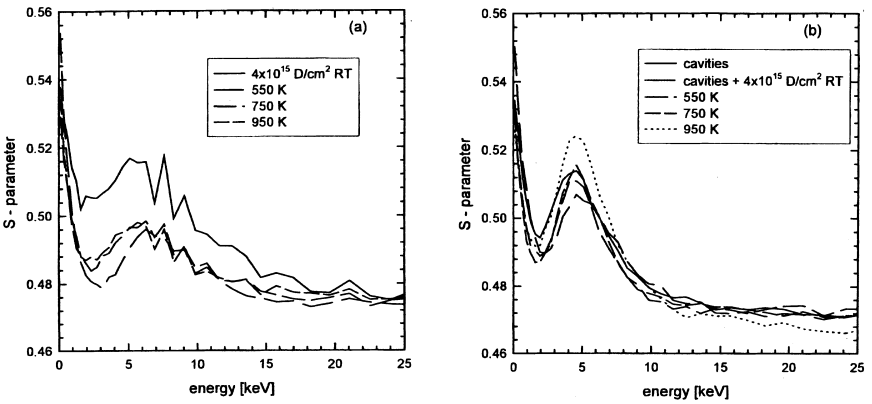

Fig. 2. S vs. E curves taken after annealing steps from RT to 950 K for samples irradiated with 4×10^{15} cm^{-2} 15 keV D^+ ions for: (a) MgO (100) with microcavities (see text); (b) virgin MgO (100).

this type of release might occur in the above annealing experiments at 550 K but only over short distances. Freund et al. report release of hydrogen at 700 K for MgO heavily doped with OH^- [11]. The formation of OD^- groups during irradiation can not be excluded and thus above release may play a role in the observed vacancy clustering process. From the above experiments it is likely that deuterium stabilizes the growing vacancy clusters at least to a temperature of 750 K. At 950 K all deuterium must have left. The cavity formation process during annealing resembles that for ^{3}He irradiated MgO [5]. However, there it was found that the helium left only at $T > 1300$ K.

6. Conclusion

It was shown that by deuterium irradiation in MgO and subsequent annealing to 950 K a layer with microcavities can be formed. Positron beam analysis proved to be a very suitable tool to provide unique depth resolved information on the vacancy clustering process.

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