Defects and Metastability
Spin Density in Thin Film Silicon Before and After Electron Bombardment

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ABSTRACT

The defect density in thin film silicon was increased using low temperature 2MeV electron irradiation up to a factor of 1000. More than 30 samples of different structure from highly crystalline to amorphous were prepared with PECVD and irradiated to study the dynamics of defect accumulation and role of the material structure in this process.

INTRODUCTION

The Electron Spin Resonance (ESR) technique is an established method for investigation of paramagnetic electrons in the defect related states in thin film silicon [1, 2]. The technique being sensitive to the nearest neighbourhood of the electron in paramagnetic state in principle might give information on the nature and configuration of the given defect [3] and not only their density. But structural disorder of the investigated material smears out fine structure of the spectrum due to inhomogeneous line broadening. Slightly asymmetric ESR lines at g-values in the range of 2.0045-2.0056 with the width of 6-8 Gauss characterize the intrinsic thin film silicon [1, 2, 4, 5, 6]. The resonance is commonly assigned to the silicon dangling bonds (db) in different environments but more specific information on the defects configuration is missing. Also the role of defects in the transport properties of the material separated from the role of the microstructure is of interest.

We apply 2MeV electron irradiation with successive annealing to the samples of thin film silicon prepared over the whole range of structural compositions in order to (i) gain additional information on the nature of defects from analysis of ESR spectra at different steps of the experiment (ii) study the role of defects in the transport properties of the material. The bombardment of thin film silicon with MeV electrons was a subject for earlier investigations [7-10] but in each case the experiment was limited to the certain material structure (a-Si:H or µc-Si:H) leaving space for a comprehensive study. Other group of studies utilizes 1-50 keV electrons for investigation of metastability of a-Si:H [11, 12] and µc-Si:H [13]. These results however should be compared to results of MeV irradiation with great caution. Since keV electrons do not produce atom displacements whereas several displacements are possible per incident 2MeV electron [14] and therefore the defect creation mechanisms are different in these two cases.

In our previous publications we reported appearance of new lines in the ESR spectra after irradiation and reversibility of radiation induced change upon annealing [15, 16]. This paper is concentrated on the spin density (N\textsubscript{s}) in the material before and after irradiation which is discussed with respect to the material structure.

Beyond the scope of our study the results presented here are of interest from the radiation stability point of view for devices made of different types of thin film silicon.
EXPERIMENT

Samples were deposited with Plasma Enhanced Chemical Vapour Deposition (PECVD) technique [17, 18] from the gas mixture of silane (SiH₄) and hydrogen. The silane to hydrogen ratio (or silane concentration - SC=SiH₄/(SiH₄+H₂) was varied in order to obtain samples with different structure from microcrystalline (2%<SC<7%) to amorphous (SC>8%). Other parameters of the deposition listed in Table 1 were constant for all samples.

Table 1. Parameters of the deposition.

<table>
<thead>
<tr>
<th>SiH₄/(SiH₄+H₂)</th>
<th>Discharge power</th>
<th>Discharge frequency</th>
<th>Substrate temperature</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-100%</td>
<td>0.1 W/cm²</td>
<td>95MHz</td>
<td>200°C</td>
<td>40 Pa</td>
</tr>
</tbody>
</table>

The samples were deposited on a 50µm thick Mo foil. The thickness of the films was in range of typically 1-3µm. The foil was bent and the flakes of the material were weighed and sealed in Wilmad 710-SQ-250M quartz tubes in atmosphere of 500hPa He for the ESR measurements.

The crystalline volume fraction of the samples was semi-quantitatively determined from Raman spectroscopy as a ratio of the integrated intensities of the Raman signal at 520cm⁻¹ and 500cm⁻¹ (attributed to the crystalline phase) and 480cm⁻¹ (attributed to the disordered phase), i.e. \( L^R \) = \((I_{500} + I_{520})/(I_{540} + I_{500} + I_{520})\) [19]. The measurements were performed on the samples on the metal foil using laser with wavelength of 647nm.

The irradiation with 2MeV electrons was performed at 100K with the electron beam current density of 5πA*cm⁻². The scheme of the irradiation procedure is presented in Fig. 1.

![Fig. 1 Schematic view of the irradiation chamber.](image-url)

The samples assembly was irradiated in flow of liquid nitrogen (LN₂) during 10 hours to acquire the dose of 1.1*10¹⁵cm⁻². The high vacuum volume of the electron beam line was separated from the volume of the irradiation chamber with an 80µm thick stainless steel foil. The beam of electrons which passed through the samples was measured with a Faraday cup for the relative control of the dose. The absolute value of the dose was determined from the
current and the cross section of the electron beam. The accelerated electrons lose energy in each medium they pass but losses in the outlet foil and nitrogen are negligible (less than 1keV) and the most attenuation takes place in the quartz tube wall where the beam loses around 200keV [20] therefore the samples indeed were exposed to the electrons of approximately 1.8MeV.

Samples were handled, transferred and stored at LN2 temperature after irradiation prior to measurements in order to prevent spontaneous annealing at room temperature.

ESR measurements are performed with conventional continuous wave technique in X band (9.3 GHz) at 40K. As one can see in Fig. 1 only the section of the quartz tube containing the sample was irradiated with electrons. Nevertheless scattered γ-rays created E’-centres [21] in the shielded part of the tube. E’-centre has a sharp and intensive ESR line that overlaps with the resonance from the sample. In order to reduce E’ concentration one end of the irradiated tube was annealed while the part of the tube containing the sample was kept in LN2 [15, 22] and shielded with Al foil. The samples were measured in the annealed part of the tube thereafter. The procedure was sufficient to reduce Ns of E’ to a negligible level.

RESULTS AND DISCUSSION

The variation of SC results in a change of the material structure as shown in Fig. 2 (a)

![Graph showing variation of SC results in a change of the material structure](image)

Fig. 2 (a) Ic-RS in the material versus SC. (b) Ns and g-value of the samples prepared over the whole range of SC. The lines are guides for the eye.

The increase of SC from 2% to 7% results in a strong reduction of Ic-RS. At SC of about 7% no crystalline contribution was detected.

In Fig. 2 (b) the g-value and Ns are plotted versus SC. The low Ns of as-deposited samples in Fig. 2 (b) demonstrates the good quality of the material. μc-Si:H has Ns=2*10^{15}cm^{-3} that decreases with decrease of crystalline volume fraction (increase of SC in the graph). The data agree well with earlier reports on device quality μc-Si:H [23]. a-Si:H after the transition (SC=9-25%) shows a minimum of Ns and corresponds to good quality a-Si:H with Ns=2.5*10^{15}cm^{-3}. Further increase of SC results in higher deposition rate (from 3 Å/s at SC=10% to 25Å/s at SC=100%) and consequently poorer quality of the material.
g-value of the ESR spectra changes through the whole range of SC from 2.0047 for highly crystalline \( \mu \text{-Si:H} \) to 2.0055 for a-Si:H prepared at SC=100%. The transition between these extremes is of interest. In particular the region where according to Raman spectroscopy the material is amorphous but g-value changes from 2.0050 to 2.0054. The region corresponds to the minimum of \( N_R \) that underlines the difference between samples of a-Si:H prepared with different SC.

The electron bombardment results in considerable changes of the ESR lineshape as shown in earlier reports [15, 16]. At the same time the position of the resonance does not change with irradiation and db-resonance dominates the spectra also after irradiation [15, 16]. Therefore we will compare \( N_R \) in as-deposited material (\( N_{SDep} \)) to \( N_R \) after irradiation (\( N_{SIRR} \)) not considering the details of the spectral shape. In Fig. 3 (a) \( N_{SDep} \) and \( N_{SIRR} \) are presented together with the ratio of these values versus SC.

![Fig. 3](image)

Fig. 3 (a) \( N_R \) in as-deposited material (black circles) and \( N_R \) after irradiation (black stars) as a function of SC. The ratio \( N_{SIRR}/N_{SDep} \) is shown with triangles. The lines are guides for the eye. (b) \( N_R \) in the irradiated material as a function of irradiation dose. Empty symbols correspond to a-Si:H with different SC, black symbols represent highly crystalline and transition \( \mu \text{-Si:H} \).

\( N_R \) increases by a factor of 50 to a factor of 1000 after irradiation depending on the material structure. In Fig. 3 (a) triangles represent the ratio \( N_{SIRR}/N_{SDep} \). The smallest relative change of \( N_R \) is observed for the \( \mu \text{-Si:H} \) with highest \( l_c^{R5}=0.8 \). The highest \( N_{SIRR}/N_{SDep} \) ratio is found in a-Si:H with SC of 10%...50% caused by the initially low \( N_R \) in this material. a-Si:H prepared with SC=100% has a smaller relative change although the absolute value of \( N_R \) is the highest after irradiation for this material type.

After irradiation one can see approximately equal values of \( N_R \) in a wide range of SC i.e. for all \( \mu \text{-Si:H} \) samples and a-Si:H up to SC=30%. At SC>30% \( N_R \) increases with increase of SC. This equity of \( N_R \) for material with different structure composition should be considered a coincidence resulting from different dynamics of defects accumulation in the respective materials. This is shown in Fig. 3 (b) where \( N_{SIRR} \) is plotted as a function of the irradiation dose. At low dose \( N_R \) of highly crystalline \( \mu \text{-Si:H} \) is significantly higher than the
value of good quality a-Si:H (SC=9%) while the dose dependence of μc-Si:H itself is more flat than for a-Si:H. Therefore at the highest dose these materials have by coincidence very similar values of N_d. This is the case for the samples shown in Fig. 3(a) that were irradiated with dose of 1.1*10^16 e/cm² (corresponds to medium dose in Fig. 3 (b)).

At any dose a-Si:H (SC=100%) prepared with high deposition rate shows almost an order of magnitude higher N_d in comparison to any other material. As we already mentioned in description of Fig. 2(a) there is a considerable difference between a-Si:H prepared with SC of 9.30% and material made of pure silane. The dose dependence of N_d for this material underlines this difference. High defect stability seems to be a characteristic feature of this material separating it from the good quality aSi:H both before and after irradiation.

The additional defects created by electron bombardment can be annealed at 160°C back to the initial value. For the details of N_d annealing see our reports [15, 16].

CONCLUSIONS

We investigated the density of paramagnetic centres in thin film silicon covering a wide range of material structure before and after low temperature electron bombardment.

The smallest relative change of N_d after electron irradiation was found in highly crystalline μc-Si:H (factor 50), whereas the biggest relative change of N_d took place in good quality a-Si:H prepared with SC of 10...30% (factor 1000). a-Si:H prepared at high deposition rate with pure silane showed the highest N_d both before and after irradiation - 10^{17} e/cm² and 3*10^{19} e/cm², respectively. The value of N_d after irradiation was an order of magnitude higher than in all other samples. This and the dose dependence in the range of 3*10^{17} ... 3*10^{19} e/cm² indicates that generated defects are more effectively stabilized in this type of material while they might more easily reconstruct in the other investigated materials.

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REFERENCE

Metastable Defects in Tritiated Amorphous Silicon

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ABSTRACT

We have observed the growth of defects caused by tritium decay in tritiated a-Si:H instead of inducing defects optically. We kept the samples in liquid nitrogen for two years. After two years the ESR signal reached ~1019 cm-3 with no evidence of saturation. However, the density is still less than the density of tritium that has decayed. We step-wise annealed (isochronally annealed) one sample up to 200 °C, where all of the defects were annealed out. Another sample was isothermally annealed at 300 K for several months. At this temperature, the defects anneal slowly.

INTRODUCTION

The appearance of optically or electrically induced defects in hydrogenated amorphous silicon (a-Si: H), especially those that contribute to the Staebler-Wronski effect [1], has been the topic of numerous studies, yet the mechanism of defect creation and annealing is far from clarified. This paper presents another method to induce silicon dangling-bond defects by replacing some of the hydrogen, H, with tritium, H. Tritium decays to He, emitting a beta particle (average energy of 5.7 keV) and an antineutrino. This reaction has a half-life of 12.5 years. The samples discussed in this paper contain approximately 7 and 10.4 at. % tritium. In these tritium-doped a-Si:H samples each beta decay will create a defect by converting a tritium, which is bonded to silicon, to an interstitial helium, leaving behind a silicon dangling bond.

We have tracked these defects through electron spin resonance (ESR) and photothermal deflection spectroscopy (PDS) [2]. The densities we measured at room temperature were smaller by orders of magnitude – only about 5x1017 cm-3. Therefore, there should exist a mechanism of defect annealing that is capable of healing ~1020 cm-3 defects at room temperature. In the present work, we extend these studies to 77K, in order to establish the saturation behavior at this temperature and the thermal stability of the Si dangling bond defects introduced by tritium decay.

EXPERIMENTAL

Both samples studied were made at the University of Toronto in 1996. The tritium gas was mixed with SiH4, and samples were deposited using a DC glow discharge deposition system at various substrate temperatures. The samples used in this experiment were deposited on glass substrates at temperatures of 423 K (150 °C) (further referred to as G181) and 498 K (225 °C)
(referred to as G83). The G181 sample used in this study was 1.5 um thick and the G83 sample used in this study was 0.26 um thick. Shortly after deposition, high temperature tritium effusion experiments determined the tritium concentration to be approximately 7.0 and 10.4 at. % in samples G181 and G83, respectively.

All ESR measurements were made using a Bruker ESR spectrometer operating at approximately 9.5 GHz with 4 gauss magnetic field modulation amplitude. ESR measures only the paramagnetic defects, such as neutral silicon dangling bonds. ESR does not measure the charged dangling bonds. Therefore, photo thermal deflection spectroscopy (PDS) was used to measure both the charged and uncharged defects in these samples at room temperature.

We expect the tritium decay to accumulate Si dangling bond defects because of the silicon-tritium bonds. The density of these defects is related to the number of tritium atoms that have decayed per unit volume. We first measured the samples 7 years after deposition, where the density of tritium atoms that had decayed since making the films was about 6x10^20 cm^-3[2]. However, both ESR and PDS measurements of the defect densities were lower by about 3 orders of magnitude because the defect density saturates at room temperature [2]. Next, we annealed the samples near the deposition temperature and kept the two samples at liquid nitrogen temperature for almost two years. During this time we used ESR to track the defect densities. After two years, the defect densities were about 10^19 cm^-3 for both samples.

After two years in liquid nitrogen, we annealed the two samples. We step-wise annealed the G83 sample at successive temperatures up to 473 K isochronally while the G181 sample was annealed isothermally at 300 K.

RESULTS AND DISCUSSION

After annealing the films, the defects began to accumulate in the dark at 77 K. The spin densities as functions of time stored at 77K are shown in Figs. 1 and 2 for samples G181 and G83, respectively. The data at the shortest times are the defect densities just after annealing. These densities are about 10^{16} cm^{-3} and 10^{17} cm^{-3} for G181 and G83, respectively. In both cases, the densities are probably due to surface or interface defects and not representative of residual densities in the bulk. The spin densities increase linearly with time. The final data points are the defect densities after about two years. In Fig. 1, the final density is about 3x10^{19} cm^{-3}, which is about 4 times lower than 1.4x10^{20} cm^{-3}, the density of tritium atoms, which have decayed since the sample was annealed. In Fig. 2, the final density is about 2x10^{19} cm^{-3}. In both samples there is no saturation in the growth as is the case at 300 K [2].