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水素プラズマ照射時の材料内欠陥のその場モニタリング
In situ monitoring of material defects during hydrogen plasma exposure

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1. Introduction

Electronic defects in semiconductor devices play important roles in the device performance and reliability [1,2]. These defects are often generated during device fabrication, where a variety of plasma processing are used for thin-film deposition, etching, dopant implantation and surface modification. Most of the defects are annihilated by post-annealing treatment. However, some defects remain in devices, restricting the device performance.

During plasma processing, the electronic defects can be generated near the material surface for several reasons, shown schematically in Fig. 1. The surface is exposed to ion bombardment, photon irradiation, radical exposure and so on. Ion bombardment may lead to surface strain and loss of matter by sputtering events, which results in the formation of defects near the surface. Some energetic ions may penetrate into certain materials, where they are neutralized and behave as impurities. The photon irradiation generates dangling bonds by breaking the weak-bonds in materials. The radical exposure is expected to generate defects, by transferring the internal energy to the surface atoms and/or chemically reacting with the lattice atoms.

2. Experiment

We prepared 4 different structures of samples by placing glass or quartz over the deposited a-Si:H film. Sample A is an uncovered a-Si:H film, and the film was therefore exposed to ions, radicals and photons generated by the plasma. Sample B is an a-Si:H film covered with glass and with a gap. The inclusion of the glass eliminates ion bombardment on the a-Si:H film. Sample C is an a-Si:H film covered with glass and sealed completely with ceramic paste. This prevents the exposure of the a-Si:H film to radicals, and the film. Sample D is an a-Si:H film covered with quartz glass and sealed with ceramic paste. The a-Si:H film was exposed to VIS, UV, and vacuum UV (VUV) photons.

The photocurrent in an a-Si:H film was then measured during the plasma treatments, and also after the treatment, i.e, the post-annealing [3,4].

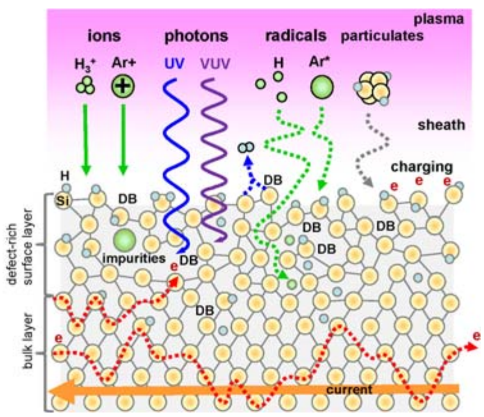

Fig. 1. Defect generation during plasma processing.

3. Results & discussion

Figure 2 shows a time evolution of the photocurrent, I_p, in an a-Si:H film for sample A during the plasma treatments and post-annealing [5]. We found that each H_2 and Ar plasma treatment caused a strong reduction in I_p, typically by one order of magnitude. The reduction in I_p began immediately after initiating the discharge/treatment; the decay time of I_p was less than 100 ms, which was limited by the lock-in time constant. The observed strong reduction indicates the generation of defects, i.e., the plasma-induced defects. Since $I_p \propto 1/n_d$, the defect density is expected to be increased by one order of magnitude during the plasma treatment.

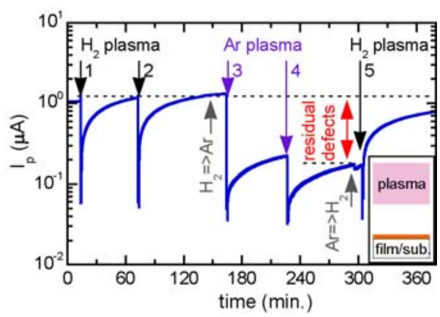

Fig. 2. Time evolution of photocurrent in a-Si:H film for sample A during plasma and post-annealing treatments [5].

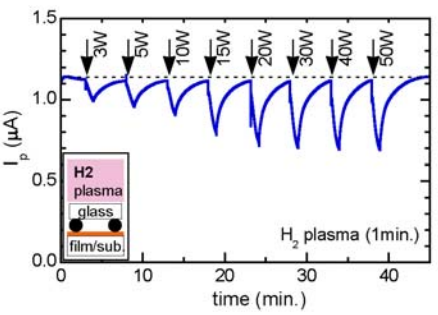

Fig. 3. Time evolution of I_p in a-Si:H film for sample C during H_2 plasma UV photon irradiation [5].

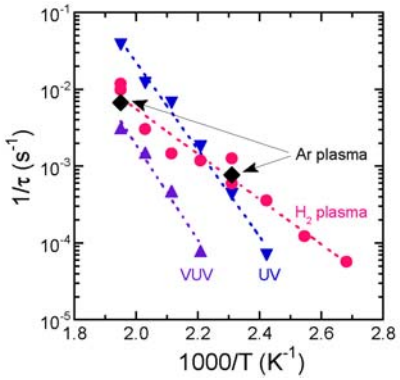

Fig. 4. Arrhenius plot for defect annihilation [5].

Once the discharge/treatment was terminated, I_p began to increase with time, showing a defect recovery trend. Interestingly, this recovery behavior of I_p was different, depending on either the H_2 or Ar plasma treatment performed before. For the H_2 plasma treatment, I_p returned completely to the initial level after annealing. On the contrary, it did not return to the initial level for Ar plasma treatment; I_p returned only 20 % of the initial level. The results suggest that the H_2 plasma-induced defects are annihilated completely by annealing, whereas the Ar plasma-induced defects are not, and some of these defects remain in the film. However, these remaining defects, i.e., the residual defects, were mostly annihilated by additional H_2 plasma and post-annealing. This result suggests that the H_2 plasma treatment is effective for the annihilation of Ar plasma-induced residual defects.

Figure 3 shows the results on I_p under the photon irradiation of a H_2 plasma at various [5]. Apparently, a reduction in I_p during the photon irradiation of a H_2 plasma was more pronounced compared with that of an Ar plasma. Increasing the power resulted in a greater reduction in I_p. This reduced I_p was again returned to the initial level by annealing. From these two experiments of the photon irradiation, we can make brief conclusions on the photon-induced defects. Firstly, the VIS photons generate less defects than those of UV photons. Secondly, the UV photon-induced defects are increased with the UV photon flux. Thirdly, the photons do not create the residual defects; the photon-induced defects are annihilated completely by annealing.

Figure 4 shows an Arrhenius plot for defect annihilation [5]. The following results are found. Firstly, $1/\tau$ shows an exponential decay on $1/\tau$, indicating that a thermal activation process plays important roles in the defect annihilation. Secondly, the exponentially decaying slope is different between the photon-induced and the plasma-induced defects; it is steeper for the photon-induced defects. To obtain the activation energy, E_a, the slope was fitted by

$1/\tau = k_0 \exp(-E_a / k_B T)$,

We found E_a =0.53±0.06 eV for the plasma-induced defects and E_a = 1.17±0.06 eV for the photon-induced defects in a range of T = 120 – 240 ^{o}C. Thirdly, the values of τ are roughly the same between H_2 and Ar plasma-induced defects at a given T although the Ar plasma treatment causes the residual defects, and the H_2 plasma treatment does not. Fourthly, k_0 is different between the UV and VUV photon-induced defects while the activation energies are nearly the same between them; k_0 is smaller for the VUV photon-induced defects.

4. Summary

We investigated the kinetics of electronic defects in a-Si:H films during H_2 and Ar plasma treatments, and post-annealing. The generation and annihilation of the electronic defects, i.e, the silicon DBs, were successfully monitored via in-situ photocurrent measurements.

Acknowledgments

The authors are grateful to Prof. M. Shiratani, Prof. K. Koga (Kyushu Univ.) and Dr. C. McDonald (AIST) for valuable discussions. This work was supported in part by JSPS KAKENHI (Grant Number 18K03603 and 15K04717).

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