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Radical, ion, and photon's effects on material damage in plasma etching

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In state-of-the-art MOSFET and memory devices, a cutting-edge plasma etching technology is widely used for device fabrication. In this fabrication, the device materials are often unintentionally damaged by plasma etching, via a strong impact of high-energy ions and an excess reaction of radicals as well as photon irradiation. The material damage is deteriorative for the device performance and reliability, so it should be suppressed. However, the damage formation and recovery mechanisms are not fully investigated. In this talk, we present the damage formation and recovery in a SiO_2/Si stack in SiO_2 etching and annealing processes. The damage is studied from a viewpoint of atomic-level defects such as dangling bonds and impurities/residues.

The plasma etching experiments are performed in capacitively coupled discharge, as shown in Fig. 1(a) [1]. A CF_4 plasma is generated by 100 MHz high-frequency discharge at 100 W at 2.0 Pa. The CF_4 plasma is characterized with optical emission spectroscopy (OES), which is shown in Fig. 1(b), indicating the presence of CF_3 and F radicals. The sample is prepared in a structure of SiO_2(109nm)/Si/SiO_2(109nm). This sample is placed on the lower electrode at room temperature, where a 2 MHz low-frequency voltage is applied to control the self-bias voltage at -300 V. After the etch experiment, the samples are H_2 gas-annealed at various temperatures of 100 ºC - 400 ºC for 30 min to study the damage/defect recovery. To characterize the damage/defects at the SiO_2/Si interface, the minority carrier lifetime of the base Si is measured with quasi-steady-state photoconductance (QSSPC) at an injection level of 1.0×10^{14}cm^{-3}.

The experimental results of the carrier lifetime, τ/τ_{ini}, after the plasma etching is shown in Fig. 2(a). As shown, the carrier lifetime strongly depends on the remaining SiO_2 layer thickness. The lifetime is reduced once the sample is exposed into CF_4 plasma for the SiO_2 etching. This lifetime reduction is clearly enhanced for thinning the remaining SiO_2 layer. This means that the SiO_2/Si interface defects are generated more for a thin remaining SiO_2 layer. On the other hand, the lifetime is increased by annealing, as shown in Fig. 2(b). This increase indicates the recovery of defects at the SiO_2/Si interface. The lifetime increase, i.e., defect recovery, is limited in a case of low-*T* annealing of 100ºC. However, the recovery is highly improved in a case of high-*T* annealing of > 200ºC. Interestingly, the defect recovery is dependent not only on the annealing temperature, but also on the remaining SiO_2 layer thickness. In a case of a thick remaining layer, e.g., d = 61.3nm, the lifetime is fully recovered at 300ºC, indicating that the defects generated during the etching are fully recovered. However, the defect recovery is limited at a relatively low level for a thin remaining SiO_2 layer, e.g., d = 23.2nm 8.2nm and 4.1nm, even at high-*T* annealing of > 200ºC. Around the endpoint, i.e., d = 2.2nm, the recovery is strongly limited at a very low level.

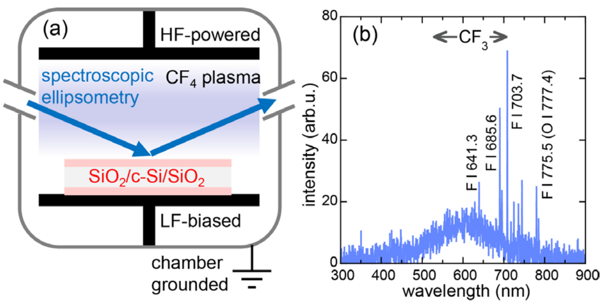

Fig. 1. (a) Experimental setup for plasma etching. (b) Optical emission spectrum of CF_4 plasma [1].

The defect generation can be explained as follows, in terms of the penetration depth and reactivity of photons, ions and radicals. For a thick SiO_2 layer, the SiO_2/Si interface defects are dominantly generated by photon irradiation, because photons penetrate deeper into the SiO_2 layer in a range of tens of nm or more. They can be absorbed at the weak bonds near the interface. This absorption may cause the dissociation of weak bonds, i.e., the generation of dangling bonds. For a thin SiO_2 layer, ions such as CF_x^+ are able to arrive at the SiO_2/Si interface, at which they may create defects in a form of strong bond formation, impurities and dangling bonds. Around the endpoint, radicals such as CF_x may play important roles in defect generation in addition to photons and ions. The CF_x radicals react with the surface Si and O atoms, yielding a reaction product of SiF_x and CO_x, which are volatile and desorbed from the surface. After the reactions, dangling bonds are created. Besides, some residues may remain on the surface. These are possible origins of residual defects.

In summary, CF_4 plasma etching-induced defects are studied at the SiO_2/Si interface. The SiO_2/Si interface defects are initially generated by photon irradiation and then by ion bombardment. Near the endpoint, the defects are also generated by radical reactions and in-diffusion. The photon-induced defects are nearly fully recovered by H_2 annealing, whereas the ion and radical-induced defects are not fully recovered.

[1] S. Nunomura et al., *Appl. Surf. Sci.* **672**, 160764 (2024).

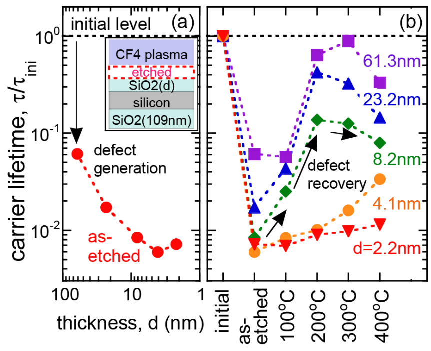

Fig. 2. (a) Carrier lifetime vs SiO_2 layer thickness. (b) Carrier lifetime vs annealing temperature [1].