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In-situ **measurements of plasma-induced defects and radical adsorption in ALE**

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The atomic layer deposition (ALD) process has been widely adopted as one of the manufacturing processes for advanced semiconductor devices, whereas the atomic layer etching (ALE) process has few applications. On the other hands, the ALE process has been expected as one of the processes to achieve damage-less and uniform processing over a wafer or inside hole. Although ALD is an effective process of forming thin films, it is not capable of depositing films with high crystallinity. Therefore, ALE will be important processes for etching while maintaining the crystalline structure of surface. Changes in crystal structure after ion bombardment have been reported by simulations, and it has been reported that ion-induced damage can extend over several layers.[1-4] However, experimental investigation has not yet been reported because surface analysis on atomic-spatial resolution without air exposure of the chemically active surface is required to observe the damage formation mechanism.

We developed a vacuum sample transfer system that can transfer clean Si surfaces between a plasma beam reactor for radical and ion irradiation and scanning tunneling microscope (STM), atomic force microscope (AFM) system without exposing the surfaces to the atmosphere. Figure 1 shows the STM image of Si (111) 7×7 surface before and after several plasma processes. Ar ion energy of 25 eV less than the sputtering threshold of Si maintained surface structure, as shown in Fig. 1 (b), 7×7 structure remained. Figure 1 (c) indicated the effect of F radicals generated in CF_4 plasma on morphology. From in-situ XPS results, it was found that the radicals irradiation formed SiF layer. F radical adsorption layer was uniformly formed, and the formed SiF layer within several atomic layers was desorbed by heating, resulting in keeping Si surface flat at atomic scale. In cyclic F radical adsorption and Ar ion irradiation process simulated ALE, however, Si (111) 7×7 surface was not observed in the STM image shown in Fig. 1 (d). The possible explanation is that synergy effect of Ar ion bombardment and F radical modification forms a mixing region including Si, F, and C atoms.

Alternatively, ALE that does not use ions bombardment for the desorption step is required.

In-situ surface measurement without air exposure of chemically active surface achieved clarifying the surface reaction mechanism in ALE. For realizing damage-less ALE, additional step is necessary to remove impurities within a few layers of Si surface or suppress ion-induced damage extending over several layers near a surface. *In-situ* observation of the formation mechanism and radical adsorption in this damaged layer is essential to understand the surface reactions for atomic layer process.

References

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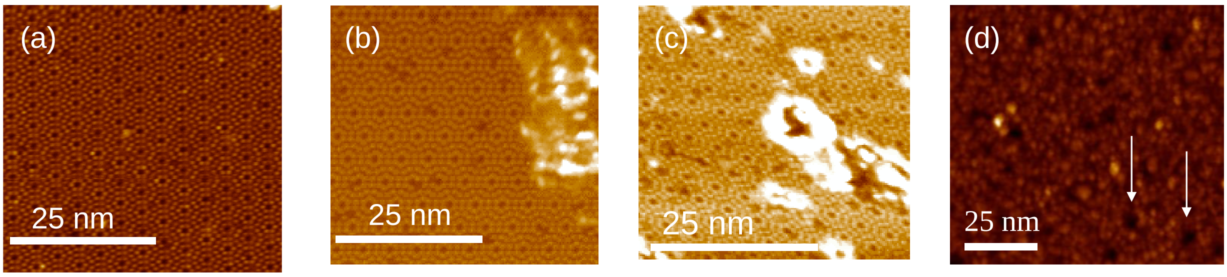

Figure 1. STM images of a Si(111) 7×7 surface (a) before plasma treatment, (b) after Ar ion irradiation with energies of 25 eV, (c) after CF_4 plasma treatment without ion irradiation, and (d) after irradiated with Ar ions after CF_4 plasma treatment, followed by annealing at 600 °C.