

**In-situ Observation of Formation of Anodic Porous Alumina Film on Si using Surface Infrared Absorption Spectroscopy**

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In recent years, there has been a growing interest in fabricating nano-scaled electronic devices (nanodevices and nanochips) on silicon in terms of innovative fabrication techniques in conjunction with matured silicon technology. Formation of nanostructured aluminum films on metal or semiconductor substrates has been extensively investigated to fabricate nanostructures on the substrates by using the porous alumina film as the template for nanostructure formation. Fabrication of such nanostructures cannot be obtained by the conventional photolithographic techniques. Therefore, we need to control precisely the anodization processes at the interfaces between the alumina and Si, and to elucidate the mechanism of anodization on the nano-scale. In this study, we have investigated the formation of porous anodic alumina film on a Si substrate using infrared absorption spectroscopy in the multiple internal reflection geometry (MIR-IRAS) and field emission scanning electron microscope (FE-SEM).

We deposited Al films with 4 μm in thickness onto a

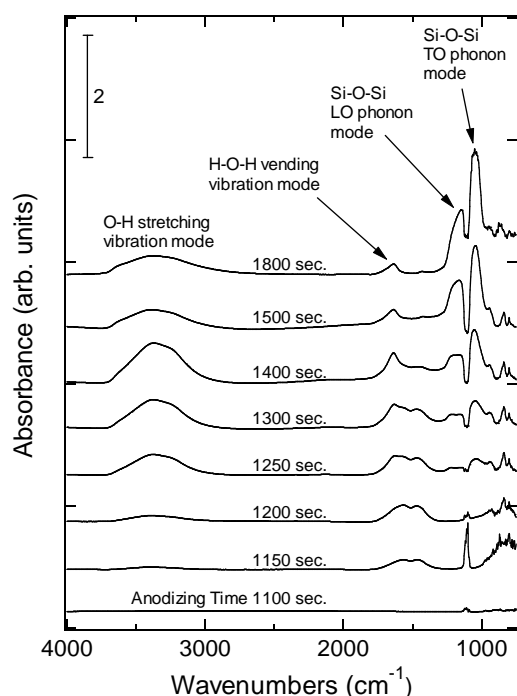


Fig. 1: IR spectral changes for an Al/Si interface during anodization.

rectangle-shaped, p-type Si(111) substrate that has a 45°-bevel on each of the short edges. IR light, which exited an interferometer (Nicolet Nexus870), was incident onto one of the short edges, propagated through the Si substrate, internally reflecting many times. The IR light that exited from the other short edge was focused on a liquid nitrogen cooled MCT (HgCdTe) detector. We used a solution cell made of Teflon™. We used an oxalic acid solution of 0.3 mol/l as the electrolyte and applied an anodic potential of 40 V to the Si substrate.

Figure 1 shows a series of IR absorption spectra collected for the Al/Si interface during anodization. IR absorption peaks at 1460 and 1570 cm<sup>-1</sup> are due to the anodic porous alumina. From the observed spectral changes we suggest that anodic porous alumina layer forms at interfacial regions close to the Si substrate; the Al layer prevents the porous anodic alumina layer from interacting with evanescent field of IR when it remains on the Si substrate surface. A broad absorption band observed around between 3400 cm<sup>-1</sup>, which is due to the O-H stretching vibration mode of the water molecule, gradually increased its intensity. This suggests that the electrolyte approached the Si substrate surface through the pores in the anodic porous alumina film. In addition, the absorption peaks due to the electrolyte and SiO<sub>2</sub> exhibited a drastic increase in intensity, when the intensity of the peak due to anodic porous alumina reached its maximum. This suggests that the electrolyte penetrated through the barrier layer between the anodic porous alumina and the Si substrate. Figure 2 shows a cross-sectional FE-SEM image of anodic porous alumina film when the penetration occurred. We can identify small holes in the barrier layers. We therefore interpret that the electrolyte penetrated through those holes and reached the Si substrate. The disappearance of the porous alumina peak shows that the alumina layer was peeled off. The peak due to the electrolyte decreased its intensity after 1500 seconds of anodization time. This suggests that Si oxides were formed and the SiO<sub>2</sub> layer prevented water from interacting with the IR evanescent field.

We carried out in-situ observation of formation of an anodic porous alumina film on Si using MIR-IRAS and observed the penetration of the electrolyte through the barrier layers. The observed IR spectral changes are consistent with the evolution of anodic current density and FE-SEM images of the anodic porous alumina film.

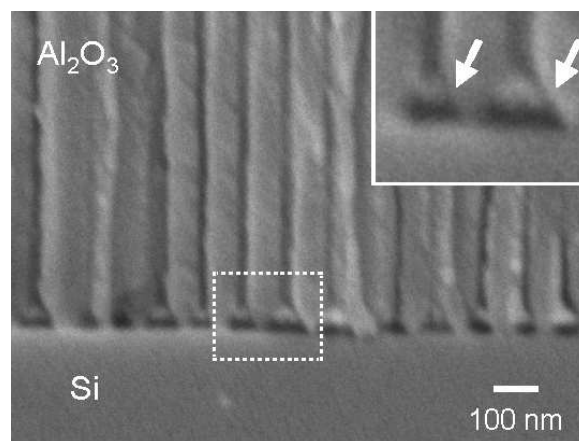


Fig. 2: A cross-sectional FE-SEM image of anodic porous alumina film when the intensity of IR absorption peak due to anodic porous alumina was the maximum.