

## Chemical-state mapping by photoelectron emission microscopy using soft X-rays

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### Introduction

For the surface analyses of various functional materials, it has become important to observe mesoscopic domains at micro- or nano-meter scale due to the rapid progress in nano-technology. Surface morphological and elemental mappings can be obtained by many kinds microscopic methods using focused electron beams. However a method for microscopic mapping dependent on the valence states has not been established. Photoelectron emission microscopy (PEEM) using synchrotron radiation is a powerful tool to identify electronic and magnetic structures at nanometer scale [1-3]. Here we report on the chemical-state mappings for silicon compounds using PEEM combined with soft X-ray excitation. The principle of the method is based on the fact that the binding energy of core electrons of an element varies with the chemical environment and chemical state by the surrounding atoms, which is called "chemical shift". The PEEM images excited by various photon energies around the Si *K*-edge were observed for Si-SiO<sub>2</sub> micro-pattern, and we have elucidated the valence states of silicon at nanometer scale.

### Experimental

The experiments were performed at the BL-27A station. The PEEM system used was Elmitech Co. Model PEEMSPECTOR. The total photoelectrons emitted from the sample surface were accelerated and focused on the YAG screen using electrostatic lenses. The images were observed by a CCD camera. The lateral spacial resolution of the system was about 41nm using an ultra-violet light source. The samples investigated were Si/SiO<sub>x</sub> micro-patterns prepared by 3 keV O<sub>2</sub><sup>+</sup> ion implantation in Si(001) wafer using a mask of 12.5 μm periodicity. The sample surface was illuminated by soft X rays around the Si *K*-edge.

### Results and discussion

Fig.1(a) shows the PEEM image excited by 1846.6eV photons. This photon energy corresponds to the resonance excitation from Si 1s to σ\* state in SiO<sub>2</sub> (σ\* resonance). It is presumed that the bright part originates from SiO<sub>2</sub>-domain, and dark part is due to the Si-domain. In order to confirm these assignments, we have measured the photon-energy dependences of the brightnesses of the spots A (dark region) and B (bright region) of fig.1(a), which are shown in fig.1(b). The near edge X-ray absorption fine structure (NEXAFS) spectra for Si(001) and SiO<sub>2</sub> are also shown as solid lines.

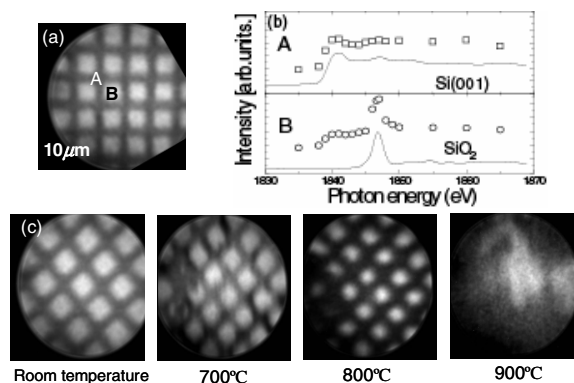


Fig.1 (a) PEEM image of Si-SiO<sub>2</sub> micro-pattern excited by 1846.6 eV photons. (b) Photon-energy dependences of the brightness of domains A and B in (a). XAFS spectra of Si and SiO<sub>2</sub> are shown as solid lines. (c) PEEM images of Si-SiO<sub>2</sub> micro-pattern heated at various temperatures.

The curves for the brightnesses of the spots A and B are similar to the NEXAFS spectra for Si(001) and SiO<sub>2</sub>, respectively. Since the changes in the brightness in PEEM images are due to the X-ray absorption intensity of the respective chemical states, we could identify the valence states of silicon at every spot in the PEEM image. The surface of this sample is topographically flat, thus it is demonstrated that the present method can be applied to the observation on the microscopic pattern depending not on the morphology but only on the valence states of silicon.

Fig.1(c) shows the in-situ observed changes in the PEEM images upon annealing. It is seen that the diffusion of oxygen begins at 800°C, and the surface becomes almost homogeneous at 900°C. We have also observed the valence states of silicon at the Si-SiO<sub>2</sub> interface during the diffusion on the basis of the photon-energy dependences of the brightnesses. As a result, we found that the diffusion of oxygen induced the sudden changes of the Si valence states from Si<sup>0</sup> to Si<sup>4+</sup> without taking any intermediate valence states.

### References

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