

## Summary

Various experimental and theoretical technologies, including X-ray photoelectron spectroscopy (XPS), high-resolution electron energy loss spectroscopy (HREELS) and density functional theory (DFT) calculations were employed to explore the thermal and photo-induced oxidation reaction on silicon and copper surfaces.  $O_2$  and  $CO_2$  are selected as the probe to adsorb onto the clean silicon surfaces, acetylene modified silicon surfaces and clean copper surfaces, and the results demonstrate that there will be different oxidation reactions on surfaces with thermal or photon activations.

The adsorptions of  $O_2$  and  $CO_2$  on the Si(111)- $7\times 7$  surface at 110 K show that both  $O_2$  and  $CO_2$  molecules can significantly oxidize the Si(111)- $7\times 7$  surface and form thin oxide films. Two oxygen species in the oxide films were identified by XPS as oxygen atoms binding to on-top sites of adatom/rest atoms at  $\sim 533$  eV, and oxygen on bridge sites of adatom/rest backbonds at  $\sim 532$  eV. These two oxygen species can be interconverted thermally during the annealing process. Due to the low oxidation capability, the silicon oxide film produced by  $CO_2$  has a lower O/Si ratio than that of  $O_2$ .

Acetylene adsorbed Si(111)- $7\times 7$  surface will form ethylene-like (Si-CH=CH-Si) species covered silicon surfaces. This surface species can be thermally activated and will react with  $O_2$  at 450 K. In this oxidation process, the =C-H bond is exclusively

activated by the thermal activation, which promotes the oxygen insertion reaction. Then a vinyl-alcohol-like ( $\text{Si-CH=C(OH)-Si}$ ) species produced and simultaneously tautomerized to acetaldehyde-like ( $\text{Si-CH}_2\text{CO-Si}$ ) species due to its poor stability. The results suggest a number of interesting topics for the further work of the functional multilayer construction on silicon surfaces.

This  $\text{Si-CH=CH-Si}$  functionality can be also selectively oxidized to an epoxide-like structure by  $\text{O}_2$  through 193 nm photon irradiation on the  $\text{Si(111)-7\times 7}$  surface at 110 K. In this process, the photons play a critical role in the exclusive  $\text{C=C}$  bond activation, which promotes the selective epoxidation reaction. Therefore, the potential of photochemical methods as powerful tools for the activation of the first organic functional layer on the silicon surface has been demonstrated.

Based on the understanding of the thermal and photon induced oxidation of chemisorbed acetylene with  $\text{O}_2$  on the  $\text{Si(111)-7\times 7}$  surface, the reaction of  $\text{CO}_2$  with  $\text{Si-CH=CH-Si}$  surface species was studied. It was found that  $\text{CO}_2$  reacts with  $\text{Si-CH=CH-Si}$  surface species through a photon induced [2+2] cycloaddition, while there is no thermal induced reaction. In the Woodward-Hoffmann rules, this [2+2] cycloaddition is symmetry forbidden unless there is photon activation. For the  $\text{Si-CH=CH-Si}$  surface species, the 193 nm photon is energetic enough to active one electron from LUMO to HOMO to improve the cycloaddition reaction with  $\text{CO}_2$ . For thermal activation, the [2+2] cycloaddition is still symmetry forbidden; meanwhile

CO<sub>2</sub> is not energetic enough to insert into the weakened =C-H bond.

The adsorption and photochemistry of CO<sub>2</sub> on ordered/disordered Cu surfaces have been investigated using XPS and HREELS. The physisorbed CO<sub>2</sub> species and chemisorbed CO<sub>2</sub><sup>δ-</sup> species can be easily isolated on the different surfaces, facilitating studies on the photochemical behaviors of physisorbed and chemisorbed species upon the 193 nm irradiation. It was found that no photoinduced reaction occurs for the physisorbed species. However, photoinduced dissociation was evidenced in the case of chemisorbed species.