

Soft X-ray Natural Circular Dichroism and Chemical Evolution of Biomolecules

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On the basis of the first successful observation of the soft X-ray natural circular dichroism SXNCD[1], we are now readjusting the measurement systems in an attempt to improve the detection sensitivity.

Here we report the experimental results on chemical evolution from amino acid to peptide, induced by 860 eV soft X-ray irradiation.

Thin films of Glycine (Gly) were prepared at Kobe University with vacuum sublimation technique[1]. Thickness of these films was determined to be about 1 μm.

Gly films were irradiated with soft X-ray at 860 eV. XANES spectra of irradiated samples were obtained by the drain current method. After completing the spectral measurement, all samples were analyzed at Kobe University by the high performance liquid chromatography in order to determine quantum yield of formation of glycol-glycine (glycine dimer, (Gly)₂) in absolute value.

Total number of absorbed photons was estimated on the basis of drain current from the post focusing mirror to be 1.5 x 10¹³ photons. Quantum yield of formation of (Gly)₂ was determined to be (3.6±0.9)x10⁻² molecules/photon.

The curve EXP in Fig. 1 shows a XANES spectrum of a Gly film irradiated at 860 eV. The vertical axis (mass absorption coefficient by K-shell electron of nitrogen) of the figure was calibrated on the basis of database by Henke et al.[2] at 422 eV.

As pointed out in our previous report[3], before irradiation, the peak at 402 eV was observed in (Gly)₂ film, nor in Gly film. Thus we concluded that the 402 eV peak was produced by 860 eV irradiation.

Assuming the peak at 402 eV is due to (Gly)₂

produced by soft X-ray irradiation, we determined the magnitude of XANES component by (Gly)₂ as shown in the figure. The magnitude of the residual XANES intensity at 407 eV was thought to be due to Gly. The curve Gly in Fig. 1 was determined on this idea. The curve CALC in the figure was obtained by the summation of curve Gly and (Gly)₂. As seen from the figure, agreement between curves EXP and CALC is good.

The magnitude ratio of (Gly)₂ to Gly curve means that 31 % of the molecules detected by XANES technique near the surface, are (Gly)₂. We tentatively concluded that the chemical evolution of amino acid might be accelerated at the surface.

References

- [1] M. Tanaka et al., Physica Scripta 2004, in print.
- [2] B. L. Henke et al., Atomic data and Nuclear Data Table, 54, 181(1993).
- [3] K. Nakagawa et al., SPring-8 User Exp. Report No. 8 (2001B), p. 116.

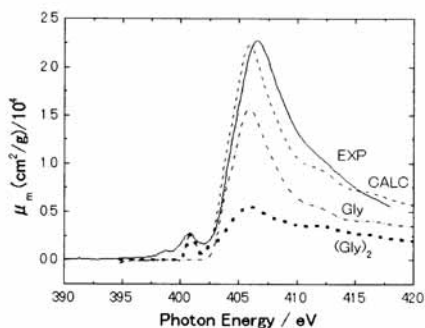


Fig.1. XANES spectrum of a glycine film irradiated with 860 eV soft X-ray. EXP: Experimental result. CALC: Calculated result (see text).

Translational Energy Effect of O₂ Molecule for Growth of Very Thin Oxide on Ti(0001) Surface

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The oxidation reaction on the Ti(0001) surface using a supersonic O₂ molecular beam was investigated by real-time photoelectron spectroscopy to clarify the O₂ adsorption mechanism and translational kinetic energy E_t effect on the growth of very thin oxides.

From the O₂ dosage dependence of O 1s photoelectron intensity, we obtained the initial sticking probability S₀ as shown in Fig.1. The S₀ decreases monotonously with increasing E_t, indicating that dissociative adsorption of O₂ molecules on the Ti(0001) surface proceeds through a physisorbed state (trapping-mediated adsorption). This reaction model is supported by the observation that the S₀ remains almost unchanged when the incident angle of a supersonic O₂ molecular beam is increased from 10° to 90°.

At E_t = 2.25 eV, the oxide thickness and oxidation state progresses very gradually after the initial rapid changes, although the oxygen

uptake increases rapidly up to 4000 L as shown in Fig. 2. At the first break in thickness (20Å), the oxidation state changes drastically from TiO to the higher oxidation states. At O₂ dosages above 6000 L, although the oxide thickness shows a saturation at ~40Å and the oxygen uptake decreases slightly, the TiO₂ component continues to increase. It is revealed that the thickness and oxidation state change depending strongly on E_t.

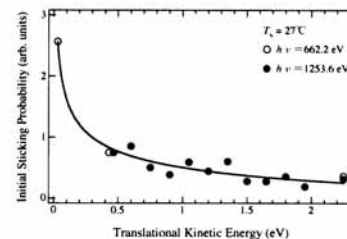


Fig. 1. Translational kinetic energy dependence of the initial sticking probability S₀ of O₂ molecule on the Ti(0001) surface measured at 27°C. The S₀ was obtained by O 1s photoelectron spectroscopy using a characteristic X-ray (hν=1253.6 eV: ●) and a synchrotron radiation (hν=662.2 eV: ○). The solid line is a guide for eyes.

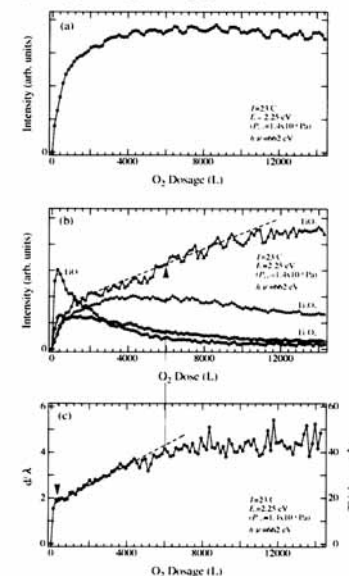


Fig. 2. O₂-dosage dependence of (a) oxygen uptake obtained from the integrated O1s intensity, (b) Ti 2p intensity for the oxidation state of TiO (●), Ti₂O₃ (○), Ti₃O₅ (△), and TiO₂ (▲), and (c) oxide thickness.