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Determination of Oxidation State of Tin by Photoemission and AES:Using SnO_x Thin Films Grown by Reactive Ion Assisted Deposition

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Highly oriented nonstoichiometric tin oxide thin films were grown by a reactive ion assisted deposition onto Si(100) and glass substrates at room temperature as a function of relative ion(O)/atom(Sn metal) arrival ratio and concurrently the deposited ion energy-per atom(eV/atom) were changed from 10 to 100 eV/atom.

As-deposited tin oxide films show preferred orientation along SnO₂<101> axis and the XRD peak intensity appears maximum at average energy of about 50 eV/atom. From quantitative Auger electron spectroscopy, characteristic transitional Auger peaks of Sn metal MNN transitions were shifted to lower kinetic energies by 4 ~ 6±1.0 eV as the Sn⁴⁺ component becomes dominant in the deposited tin oxide films and the position of O KL₁₂L₂₃ transition line was also shifted to lower kinetic energy by 1 ~ 2±1.0 eV as the composition of deposited tin oxide films were changed from SnO to SnO₂, respectively.

On the basis of Sn 3d, O1s core-level and Sn 4d near core-level spectra analysis by x-ray photoelectron spectroscopy, the sizable chemical shift of different valencies between stannous tin(Sn²⁺:SnO) and stannic tin(Sn⁴⁺:SnO₂) were 1.0±0.02 eV and that of O1s was 0.87±0.02 eV, and those values show larger shifts than previously reported value of 0.7 eV.

The valence-band was investigated by angle-resolved UPS using He(I) discharge source. The ARUPS results agree well with previous studies on SnO₂(110) single crystal and polycrystalline tin oxide surface. Our spectra reveal a general VB width of 12.5 eV and the main peaks at 5.5 eV, 10.5 eV and 13 eV. Decreasing oxygen surface concentration leads to band bending toward the Fermi level. The intermediate state and lower part of the VB show large dispersion due to the strong interaction between Sn 5s, 5p orbitals and O 2p orbital.