Study of Nano-Space in Au-Polysilane Interfaces by Slow Positron Beam

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One of the most crucial factors disturbing the electro-luminescence (EL) characteristics of polysilanes is the formation and accumulation of defect structures of their Si skeletons at the interface between polysilanes and electron injecting electrodes (EIE)[1,2]. The defects at the interface are generated either during polymerization or fabrication of the LEDs, and the former has been quantitatively investigated by a variety of techniques. However there was no direct evidences suggesting the formation and accumulation of the defect structures induced by the fabrication processes of LEDs, especially the formation of EIE by evaporation of thin metallic films on polysilanes.

Positron annihilation lifetime spectroscopy (PALS) is very powerful technique to probe free volumes in polymers. We discuss the direct observation of defects at the Au-polysilane interfaces by PALS using slow positron beams.

Poly(methylphenylsilane) (PMPS) was prepared from corresponding monomers as methylphenyldichlorosilane which was purchased from Shin-Etsu chemical Co. LTD. Monomer was distilled twice prior to use. Polymerization was carried out by the conventional sodium condensation method [3]. Obtained polymers were precipitated using isopropyl alcohol after filtration to roughly remove NaCl, and the precipitates were dried under vacuum, respectively. The polymers were washed by water, and precipitated with tetrahydrofuran-isopropyl alcohol mixture. The molecular weight distributions in these polymers were also measured with a Shimadzu LC-10A gel permeation chromatography (GPC) system with polystyrene calibration standards. The

values of number and weight average molecular weights (M_n and M_w) was 2.2×10^4 and 4.5×10^4 . PMPS was coated on Si substrates with 1 μm thick, and Au semitransparent EIE layers were overcoated by evaporation with 20 nm thick.

Positron lifetime measurements were carried out as a function of positron energy (30 eV – 7 keV) using the LINAC based positron beam facility at Osaka University [4]. Instrumental time resolution function is about ~290 ps (FWHM) using PATFIT program [5]. Each positron annihilation lifetime spectrum contains half million counts.

Data analysis was carried out using PATFIT program. The positron lifetime and correlating intensity were evaluated. The free volume radius R is given by the following equation as a function of τ_3 ,

$$\tau_3 = \frac{1}{2} \left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin \left(\frac{2\pi R}{R + \Delta R} \right) \right]^{-1}$$

where τ_3 is *o*-Ps pick-off lifetime (ns), R the radius of free volume hole (nm), $R + \Delta R$ the radius of hypothetical spherical well where Ps exist, and ΔR the homogeneous electron layer thickness which is the empirical parameter of 0.166 nm fitted from *o*-Ps lifetime measurement of known cavity size [6].

PALS experiments are performed as a function of implantation positron energy. Positron annihilation lifetime spectra are fitted into two lifetimes using PATFIT program. Longer lifetime component ascribed to *o*-Ps pick-off annihilation can be resolved. Figure 1 shows *o*-Ps lifetime and intensity vs. positron incident energy for PMPS and Au-PMPS. The incident positron energy can be correlated with the

mean implantation depth $z(E)$ (nm) as $z(E)=40E^{1.6}/\rho$, where E and ρ are the positron incident energy (keV) and material density (g/cm^3), respectively. The positron implantation depth profile has larger distribution as the positron incident energy increases, which is known as Makhov function, described elsewhere [7]. The mean implantation depths are indicated in respective figures. The o -Ps lifetime is almost same at **PMPS** and **Au-PMPS**. Therefore, defect size in **PMPS** is not affected by vacuum evaporation of Au. However, the o -Ps intensity in **Au-PMPS** is higher than that in **PMPS**. The influence attains to **PMPS** bulk layer as deep as 700 nm from the surface.

We consider the process of chemical structural changes caused by metal cluster bombardment on **PMPS**. Recently, Maeda [8] reported that cross-linking and main chain scission reaction in **PMPS** by irradiations. This report shows that a

number of phenyl scission reaction is larger than that of alkyl substituents including CH_3 upon irradiation to γ -rays. This implies that highly efficient dissociation of phenyl ring from the backbone is caused by vacuum Au evaporation. The effects of Au evaporation on **PMPS** were also reported by Nagayama et al.[9] Au thin layer evaporated on a **PMPS** film after exposure to UV-light led to the formation of Au colloid embedded in **PMPS** upon heating, and the colloid formation was not observed for polysilanes without phenyl substituents. This process is predominantly promoted by the degradation of **PMPS** by catalytic oxidation due to the colloidal Au, however, the role of phenyl rings and the diffusion of formed colloids into **PMPS** bulk indicate good correspondence to the present results. We conclude that defect structures in phenyl-substituted polysilane are especially affected by vacuum evaporation of Au, and that the influence attains to bulk as deep as 700 nm from surface.

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Figure1. o -Ps lifetime and intensity vs. positron incident energy for **PMPS** and **Au-PMPS**. Opened circles indicate the **PMPS**, closed squares indicate the **Au-PMPS**. Positron mean implantation depth is shown in upper horizontal axis.