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Abstract: Vapor deposited short chain polyaniline thin films were studied using angle-resolved photoemission spectroscopy. Films grown on two different substrates, oxidized Si surfaces and Au, show distinctly different properties. Some indication of preferential molecular orientation was observed for ultrathin films deposited on Au substrates, but not on the Si substrates with the native oxide surface. Clear indication of metallic character was observed for some of the polyaniline ultrathin films, consistent with recent theory suggesting that alignment of chains parallel with a metal substrate enhance metallicity. © 2002 American Vacuum Society.

Among the conducting polymers, polyaniline has generated considerable interest in the past several years due to its environmental stability, the easily controlled electrical conductivity, as well as for the possible applications in sensors and microelectronic devices.[1–5] Polyaniline films are generally produced from solution by chemical or electrochemical methods,[5,6] but such films are generally not amenable to studies of the interfaces and often some solvent remains within the films. It has been demonstrated that polyaniline thin films can be produced by vapor deposition[7–10] and the resulting films, deposited mostly on noble metal substrates, have been extensively studied by high resolution electron energy loss spectroscopy,[9] complemented by a very few scanning tunneling microscopy/atomic force microscopy (AFM) studies.[10,11] Although it is the states near the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap that dominate the optical and conduction properties of polyaniline,[1, 7, 8, 12–14] few valence band photoemission studies have been undertaken.[12,15] The optical cross section of such states and excitations across the HOMO-LUMO gap (including optical conductivity) can be influenced by dipole and symmetry selection rules, particularly if there is preferential ordering in the deposited short chain polyaniline.

The samples were prepared in a vacuum deposition system. The polymer evaporation source consisted of a quartz Knudsen cell filled with emeraldine base powder (Aldrich) which was resistively heated to 650 K. The thickness of the films was monitored by a thin film monitor placed near the substrate. The angle-resolved photoemission spectroscopy experiments were performed on the 3 m toroidal grating monochromator at the Center for Advanced Microstructures and Devices (CAMD) and the photoemission spectra were undertaken using a 50 mm radius hemispherical electron energy analyzer with an angular acceptance of ±1.5°. The photoemission spectra were taken at several different photon energies to test for two dimensionality of state, though the spectra reproduced here were taken with a photon energy of 70 eV. The

system pressure during the experiment was better than 2×10^{10} Torr.

We studied vapor deposited polyaniline thin films with the aim of investigating the possible preferential bonding orientation in vapor deposited polyaniline and resulting light polarization effects in photoemission. Three different vapor deposited polyaniline thin films were investigated: polyaniline films with thickness less than 50 Å and thicker than 100 Å on Au-coated (500 Å) Si(111) substrates [Figs. 1(a) and 1(b), respectively] as well as films deposited on degenerately B doped Si(111) substrates with a native oxide surface [Fig. 1(c)]. Silicon substrates, with the high doping level, were chosen to ensure sufficient conduction of the substrate. The thickness of Au films on Si(111) was estimated from the deposition rate of the e-beam evaporator. Roughness of Au films was generally smaller than 10 Å, based on AFM and scanning electron microscopy (SEM) measurements, and no Au islands were resolved. The Au surface state was observed in the photoemission valence band structure suggesting little surface contamination, and there was no evidence of pinholes in the Au film in photoemission.

In every panel of Fig. 1, two different photon incident angles were used: the red spectra are with light incident angles of 40° off the surface normal (s + p-polarized light), the blue spectra are with light incident angles of 65° off the surface normal (p-polarized light). To retain the highest point group symmetry, the photoelectrons were collected along the surface normal. The difference spectra between the two incident angles (s + p polarization minus p polarization) are shown at the bottom of each panel.

For the thinner films on gold, the HOMO band and near HOMO bands are enhanced in s-polarized light. Based upon the calculated band structure of polyaniline,[12, 13, 14] we have followed the assignment of Barta et al.[12] in attributing the photoemission features to the various occupied bands, as indicated in Fig. 1. The HOMO, HOMO-1 and HOMO-2 should all be observed in both p- and s-polarized light, but should be more strongly observed, by far, in s-polarized light if the mo-
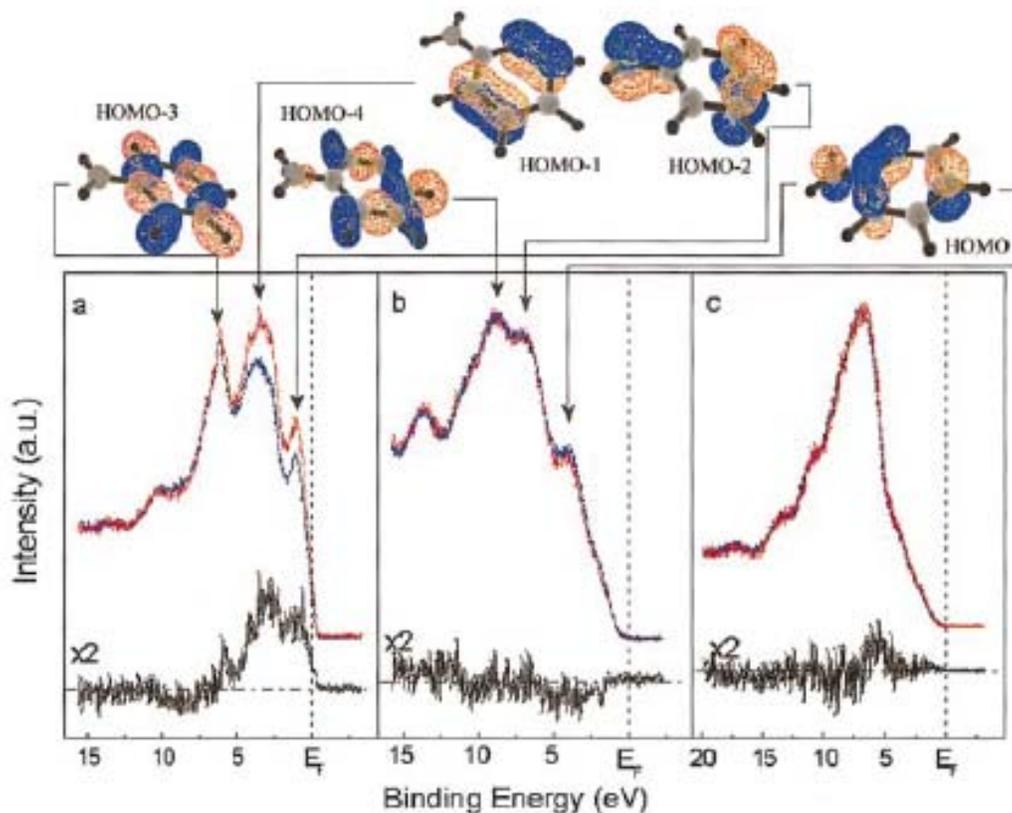
FIG. 1. Angle-resolved photoemission spectra of vapor deposited polyaniline films with thickness less than 50 Å and thicker than 100 Å on Au-coated (500 Å) silicon substrates [(a) and (b), respectively] as well as films deposited on silicon substrates with a native oxide surface (c). In every panel, two different photon incident angles were used: the red spectra are with light incident angles of 40° off the surface normal (s + p-polarized light), the blue spectra are with light incident angles of 65° off the surface normal (p-polarized light). The difference spectra between the two incident angles (s + p polarization minus p polarization) are shown at the bottom of each panel. Simplified (based on aniline alone) schematic representations of the HOMO, the overlapping HOMO-1 and HOMO-2, and the overlapping HOMO-3 and HOMO-4 photoemission features are indicated as an inset.

lecular plane and chain axis are both parallel with the surface. The HOMO-3 band would be enhanced in s-polarized light, but the HOMO-4 band would be difficult to observe in s-polarized light in such a molecular geometry. These expectations, for the aromatic ring plane and chain axis both largely parallel with the surface, are consistent with experiment. The absence of strong enhancement in p-polarized light and photon energy dependence in the photoemission spectra provides a strong argument against a molecular configuration with the chain axis along the surface normal. We observed no temperature dependent changes in the symmetry dependence or photoemission spectra of vapor deposited polyaniline films on Au (and there was no evidence of surface photovoltage effects or surface charging, either). This is distinctly different from what was found for thin films of polypyrrole, doped with perchlorate (ClO4–).[15]

While the phenylene rings of polyaniline (and the chain) are oriented largely parallel with the surface (for the thinner vapor deposited polyaniline films), small tilt angles, suggested by the observed vibration modes,[9] cannot be excluded from the data presented here, and small alternating cant angles from one aromatic ring to the next are expected from

the native structure of polyaniline. The diminished enhancement of the HOMO, HOMO-1, and HOMO-2 bands, in s-polarized light [Fig. 1(b)], suggests that with increasing thickness of polyaniline on gold, the phenylene rings tend to tilt out of the plane. The results are consistent with the STM results for long chain polyaniline thin film crystal, previously reported.[11] The conductance of polymer π-conjugated ring system is expected to strongly depend on substrate interactions from recent theoretical work. The π-conjugated polymer systems, coplanar with the substrate, are expected to exhibit much higher conductance.[16] This is consistent with a shift of polyaniline molecular orbitals towards the Fermi level in the thinner films as seen from Fig. 1.

It is well established that the orientation and chemical bonding of large organic adsorbates depend strongly on the properties of the substrate surface[17–20] and the thickness of the films.[20, 21] The differences observed, between polyaniline adsorption on gold and surface oxidized silicon, are expected. In the case of Au-coated substrate, the weak interaction between the gold and polyaniline π-conjugated system permits the adsorbates to lie more or less flat on the surface, so a general preferential molecular orientation is possible, as

is indicated by the results presented here. With the increasing film thickness, the interaction between gold and polyaniline decreases. This leads to the disappearance of the polarization dependence of the density of states as the polyaniline "plane" can more easily tilt out the plane of the surface. With silicon, covered by a native oxide, mobility is suppressed in favor of a variety of molecular orientations, possibly complicated with a heterogeneous variety of postdeposition reactions,[8] thus obscuring any observation of a preferential molecular chain or bonding orientation. Such reactions, that include oxygen incorporation into the film or deprotination reactions, are known to substantially lower the conductivity of polyaniline.[8] This is consistent with the strong shift to higher binding energies of the polyaniline molecular orbitals in Fig. 1(c) (most likely due to final effects) and the lower density of states, not only at E_F but also at the valence band edge [Fig. 1(c)].

The electrons generally appear delocalized in conjugated systems. For the ultrathin film on Au-coated substrate, the existence of "planar" preferential orientation of polyaniline enhances the delocalization of the electrons, which should lead to a greater conductivity. On the other hand, for the other two films where there was less or no preferential polyaniline orientation, the photoemission evidence suggests that electron itinerary will be small, and the HOMO-LUMO gap opens to a greater extent. The photoemission peak widths are greatest for the sample most likely to be heterogeneous: polyaniline on oxidized Si. The narrowest photoemission peak widths are observed for the thinner polyaniline films on Au-coated substrate: the polyaniline films with the strongest preferential orientation and are the least likely to exhibit heterogeneous postdeposition cross-linking.

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