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Professor Hai-Lung Dai

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Chemistry
University of Pennsylvania
231 South 34th Street
Philadelphia PA 199104-6323

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14. ABSTRACT

Toward the goal of developing fundamental understanding of structural properties of molecular thin films to form a scientific basis for designing and preparation of molecular thin film materials, we have made important advances during the past three years. These advances were enabled through applying a combination of ultrahigh vacuum surface science and nonlinear optical techniques to the characterization of thin molecular films. Specifically we have demonstrated for the first time that the nonlinear optical technique Second Harmonic Generation can be used to determine the geometric structure of the interfacial layer of mulecules buried in between the molecular film and the solid substrate, and that surface-state enhanced SHG can be used to probe the wetting-dewetting transition of monolayer molecular adsorbates on a metal. The nature of bonding between the layer of linear acenes, molecules such as tetracene and pentacene that have great potential as organic semiconducting materials, have been determined. Overall, we have gained to great extend a fundamental understanding of molecular film deposition, growth, and crystallization mechanisms. This research effort has resulted in a total of 13 referred publications since 2004 to date (listed at the end of the report). A more detailed description of research results are presented below.

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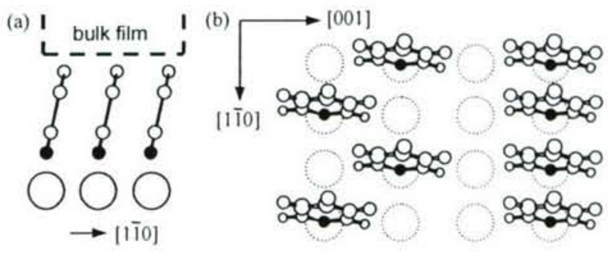
Toward the goal of developing fundamental understanding of structural properties of molecular thin films to form a scientific basis for designing and preparation of molecular thin film materials, we have made important advances during the past three years. These advances were enabled through applying a combination of ultrahigh vacuum surface science and nonlinear optical techniques to the characterization of thin molecular films. Specifically we have demonstrated for the first time that the nonlinear optical technique Second Harmonic Generation can be used to determine the geometric structure of the interfacial layer of molecules buried in between the molecular film and the solid substrate, and that surface-state enhanced SHG can be used to probe the wetting-dewetting transition of monolayer molecular adsorbates on a metal. The nature of bonding between the layer of linear acenes, molecules such as tetracene and pentacene that have great potential as organic semiconducting materials, have been determined. Overall, we have gained to great extend a fundamental understanding of molecular film deposition, growth, and crystallization mechanisms. This research effort has resulted in a total of 13 referred publications since 2004 to date (listed at the end of the report). A more detailed description of research results are presented below:

A. Determination of the structure of the interfacial layer between a thin molecular film and the metal substrate

It is demonstrated that by using SHG the orientation and alignment of molecules in the interfacial layer between two solids, a thin solid molecular film and a metal substrate, can be determined. As shown in the figure, the pyridine molecules in the interfacial layer underneath the film are found to align, with a 5° rotation angle, along the [1$\bar{1}$0] direction of the Ag(110) surface. The tilt angle of the molecular principal axis from the surface norm has been determined to be ~11°. This



interfacial ordering is found to have a notable effect in inducing pre-crystallization at the heterogeneous boundary of the amorphous molecular film.

B. Adsorption, bonding and intermolecular interaction of mono- and multi-layer linear acenes on metal

A systematic study of adsorption of linear acenes, from benzene to pentacene, on metal surfaces has been conducted. From the study of the series of molecules a generic picture of adsorption is emerging: The linear acene molecule adsorbs likely in a flat configuration allowing charge transfer bonding to the metal. On Ag, each aromatic ring transfers ~0.1 e and contributes ~10 kcal/mole to the binding energy. The local dipole moment induced by the charge transfer bonding causes strong repulsive inter-molecular interactions.

The adsorption of monolayer and multilayer benzene on the Ag(111) surface was characterized using Temperature Programmed Desorption. Analyses of TPD spectra revealed two different binding geometries on threefold-hollow sites with symmetries $C_{3v}(\sigma_d)$ and $C_{3v}(\sigma_v)$. The TPD peak analysis incorporated inter-adsorbate repulsive interaction resulted from local dipole moment at the adsorption site induced by the adsorbate-surface charge transfer bonding. The analysis has yielded desorption energies of 54.9±0.8 kJ/mole and 50.4±0.4 kJ/mole for the $C_{3v}(\sigma_d)$ and $C_{3v}(\sigma_v)$ configurations, respectively. The interface dipole and polarizability of the benzene-silver complex have been determined to be 5.4±1.8 D and 14±10 $Å^3$ respectively. Repulsive interactions in the monolayer were found to lower desorption energy from the zero-coverage value by 14.8 kJ/mole. Leading edge analysis of the multi-layer peak yielded a desorption energy of 40.9±0.7 kJ/mole for the upper layers.

The adsorption of submonolayer aniline on Ag(111) has been characterized using TPD and electron energy loss spectroscopy (EELS). Analysis of the TPD curves yielded a desorption energy of 74 kJ/mole and revealed repulsive inter-adsorbate interactions resulting from a local dipole moment of 4.3 D at the adsorbate-substrate complex. This dipole moment arises from a weak charge transfer from aniline to silver in forming the adsorption bond. Analysis of the EELS spectrum revealed several vibrational modes that are consistent with weakly chemisorbed aniline with the amino group bound to the surface. Intensity analysis based on IR selection rules on metal shows that the molecule adsorbs flatly with a small tilt angle (13±8° between the CN bond and the surface) and a small orientation angle.

The adsorption kinetics, energetics and growth of naphthalene thin films, from submonolyer to about 10 layers, on a Ag(111) surface at low temperature in a UHV chamber are examined by using TPD. The first layer adsorption occurs with a desorption energy of 85±5 kJ/mole and results in an interface dipole of 5±1 D, from charge transfer of approximately 0.2 e from naphthalene to Ag. The surface dipole induced inter-adsorbate repulsion causes the lowering of the adsorption energy within the first layer near the saturation coverage so that the second layer deposition begins before the completion of the first layer. The 2nd layer is a metastable phase with desorption energy, 74±3 kJ/mole, smaller than the multilayer desorption energy of 79±5 kJ/mole. Fractional order desorption kinetics were found for both the metastable and the multilayer phases, suggesting desorption from 2-D islanding and 3-D islanding respectively.

TPD is used for examining surface binding, inter-molecular interaction, and structure of mono- and multi-layer films of tetracene on Ag(111). TPD of monolayer tetracene revealed strong inter-adsorbate repulsion caused by interaction among interface dipoles resulted from charge transfer bonding. A modified Albano model, in which each of the aromatic ring of tetracene is assigned a point interface dipole, is proposed to account for the interfacial dipole interaction at short range. It is found that desorption energy at the zero-coverage limit is 143±7 kJ/mole. The interface dipole is determined as 10±1 D, which corresponds to a charge transfer of 0.45 e per tetracene molecule to Ag. At full monolayer coverage the strong inter-adsorbate repulsion reduces the desorption energy to 103 kJ/mole. Annealing at elevated temperature (350-400 K) but below desorption temperature on minute time scale followed by cooling appears to produce a more stable structure. Multilayer TPD spectra shows three separate half-order desorption peaks that merge into one bulk peak at higher coverage. The half-order kinetics agrees with the previously reported Stranski-Krastanov growth mode in which islands with high height-to-width ratio are formed. Desorption energies for these peaks are 100±7, 110±10, and 116±4 kJ/mole respectively. Upon annealing, the lower energy structures transform into the higher energy ones.

C. Development of nonlinear and linear optical techniques for probing wetting - dewetting, nucleation and crystallization of thin molecular films on a metal surface

Linear and nonlinear optical techniques are applied to the study of dynamical and structural properties of monolayer molecules and bulk molecular thin films on a metal surface.

The resonance enhancement of SHG from a bare Ag(110) surface due to electronic transitions between surface states is first characterized. A quantum mechanical treatment of the second order susceptibility of the Ag surface has been developed for quantitative description of changes in resonant SH intensity due to temperature and adsorbate effects on surface state energies. A fit of the experimental SH intensity to the model allows information on the relaxation dynamics of the surface state electrons to be extracted. By exploiting surface state resonant SHG as a highly sensitive probe of surface coverage we are able to monitor in real time the adsorption and desorption of a single monolayer of water on the Ag(110) surface and reveal the existence of a wetting / dewetting transition at 133.5 K.

The structure and dynamics of bulk amorphous solid and supercooled liquid molecular thin films are probed using linear and nonlinear optical techniques. SHG in combination with Rayleigh scattering exposes the sudden formation of small heterogeneous domains in water and methanol films at particular deposition temperatures. Linear reflectivity is used to identify numerous stable and metastable phases of methanol. The thermal pathway, with respect to the glass transition temperature, T_g, is important in determining film structure since the slow dynamics near T_g produce a memory effect. Furthermore, a crystallization transition to a metastable state is observed below the true crystallization. This additional transition occurs only in films deposited at temperatures below their onset of heterogeneity. The kinetics of methanol crystallization near the glass transition temperature are investigated and an abrupt change in the nucleation mechanism at T_g is observed. Finally, reflectivity reveals that water films grown at temperatures above the onset of heterogeneity access a new and distinct state of amorphous water. This heterogeneous amorphous phase appears to be more stable than cubic ice as evidenced by its higher desorption activation energy.

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