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1. REPORT DATE (DD-MM-YYYY) 27-09-2004		2. REPORT TYPE Final Performance Report		3. DATES COVERED (From - To) Sept. 1, 2001- June 30, 2004	
4. TITLE AND SUBTITLE Structure and Reactivity within Ultrathin Molecular Films				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER AFOSR Grant # F49620-01-1-0517	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Hai-Lung Dai, Department of Chemistry, University of Pennsylvania				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Pennsylvania, Philadelphia, PA 19104-6323				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research Program Officer: Michael R. Berman 4015 Wilson Blvd., Rm 713 Arlington VA 22203-1954				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT DTIC Approve for public release: distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT A new technique based on the nonlinear optical phenomenon- second harmonic generation- has been developed for probing the structure of nano- to micrometer thickness thin films made of small and medium size organic molecules. It was found that the magnitude of the inter-molecular interaction plays a critical role in determining the growth mechanism, structure, crystallization kinetics, and phase transitions of the thin molecular films. The nonlinear optical technique can even allow the determination of the orientation and alignment of the molecules at the interface between the thin film and the substrate. Order of the molecules in the interfacial layer affects the crystallization mechanism in the thin film.					
15. SUBJECT TERMS Molecular thin films, nonlinear optics, surface and interface structure and analysis					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT 100-200 words	18. NUMBER OF PAGES 6	19a. NAME OF RESPONSIBLE PERSON Hai-Lung Dai
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (include area code) 215-898-5077

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Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

20041012 040

Final Performance Report for AFOSR Grant # F49620-01-1-0517

“Structure and Reactivity within Ultrathin Molecular Films”

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Abstract:

A new technique based on the nonlinear optical phenomenon- second harmonic generation- has been developed for probing the structure of nano- to micrometer thickness thin films made of small and medium size organic molecules. It was found that the magnitude of the intermolecular interaction plays a critical role in determining the growth mechanism, structure, crystallization kinetics, and phase transitions of the thin molecular films. The nonlinear optical technique can even allow the determination of the orientation and alignment of the molecules at the interface between the thin film and the substrate. Order of the molecules in the interfacial layer affects the crystallization mechanism in the thin film.

I. Accomplished objectives

Ultrathin molecular films with nanometer to micrometer thickness have become an important class of materials because of a wide range of potential applications in modern technology such as organic semiconductors, sensors, displays, and composite materials. However, very little is known about their structure, growth mechanism and physical and chemical properties due to limited availability of experimental means for probing the thin molecular films. Consequently, much still needs to be learned about the structure and the most important factors controlling the deposition of thin molecular films. With the support of this AFOSR grant, we have developed the nonlinear optical phenomenon- second harmonic generation- as an effective experimental means for characterizing the structure, phase transitions and growth mechanisms within the ultrathin molecular films. We have demonstrated that crystallization kinetics and the crystallites within the thin molecular films, and even the structure of the interfacial layer at the film boundary can be determined. Our studies combining the nonlinear optical approach and ultrahigh vacuum surface science techniques have revealed the most important criteria for controlling the deposition and growth of ultrathin molecular

films. This knowledge will assist in the design and production of devices that incorporate ultrathin molecular films with specific properties.

II. Development of Second Harmonic Generation (SHG) as an effective experimental approach for the study of ultrathin molecular films

The molecular thin films of small and medium size organic molecules are normally prepared under vacuum conditions with temperature and purity control. The particle scattering techniques that are most effective for surface analysis under vacuum conditions, however, are ineffective for thin films studies as the penetration depth for particles such as electrons, ions and He atoms is relatively shallow. SHG as an optical technique, on the other hands, has the ability to probe underneath the surface. Furthermore, nonlinear optical phenomenon like SHG is uniquely sensitive to the symmetry of the medium, which forms the basis for probing the structure of the molecular film. Consider a molecule that has no center of inversion and will be able to generate second harmonic light upon irradiation. The nonlinear optical susceptibility of the ensemble of molecules depends on the collective sum of the individual molecule nonlinear polarization. As a result, an ensemble of randomly oriented molecules would have no SHG. But a crystalline structure without center of inversion symmetry will produce SHG. Publication 5 shows SHG detection of such an order-disorder transition. Upon heating the amorphous pyridine film deposited at 90 K is found to crystallize at $T > 120$ K. Furthermore, the symmetry of the crystallites can be resolved from the SHG spatial polarization dependence. And SH light generated at the film-substrate interface can be used to determine the film thickness and growth rate based on interference effect. This nonlinear optical spectroscopic technique, in combination with the conventional surface science techniques, provides a powerful set of tools for characterizing molecular films.

In a related development, we have demonstrated that SHG resonantly enhanced by surface state transition can be used for probing the adsorption and relaxation dynamics of monolayers on metal surfaces. Publication 3 shows that the temperature dependence of SHG resonantly enhanced by a surface state transition can be quantitatively described by a quantum mechanical model and allows the determination of the relaxation dynamics of the surface electrons. The sensitivity of the surface state electrons to adsorbate can be used for detecting adsorption with extremely high sensitivity, as demonstrated by Publication 8.

III. Fundamental Understanding of Structure and Phase Transition in Ultrathin Molecular Films

Molecules with different strength of inter-molecular interactions, such as pyridine, aniline, and water, have been chosen as model systems for study for the understanding of the effect of inter-molecular potential on growth mechanism and structure. For example, stronger intermolecular interaction restricts molecular diffusion and is expected to result in layer-by-layer growth of the film, whereas weaker intermolecular interaction allows molecular diffusion so that the film is formed through a metastable phase. Our study of the model systems has revealed the importance of inter-molecular interactions in affecting the deposition and preparation of films with desired structures. The following is a summary of specific findings achieved:

Layer-by-Layer Structure in Ultrathin Aniline and Pyridine Films on a Ag(111) Surface

Ultrathin (1-10 layers) aniline and pyridine films deposited on a Ag(111) surface at 90 K have been examined using Thermal Programmed Desorption (TPD). Multiple desorption peaks have been observed for both systems showing film growth from the first chemisorbed layer to the bulk structure through intermediate layers. The growth mechanisms for the two systems are, however, apparently different. Aniline films are formed one layer at a time with five thermodynamically stable layers (Publication 1 is the first time such layered structure is reported), as indicated by the five distinct TPD peak. In contrast, pyridine films grow through metastable phases. The difference in film growth mechanisms is attributed to intermolecular interactions.

Crystallization and Premelting in Thin Films of Weakly Interacting Molecules: A Study of Pyridine Films on Ag by Optical Second Harmonic Generation

It is demonstrated that Second Harmonic Generation from a thin molecular film can be used for characterizing the crystallization rate and premelting kinetics of the crystallites in the film. The experimental observations in Publications 5 and 6 provide a model understanding of the growth and crystallization mechanism in thin films made of molecules, such as pyridine, with weak intermolecular interactions. The crystallization rate measurements show that amorphous pyridine films, with thickness lower than 100 nm, deposited at 82 K under UHV conditions on Ag(111) are found to crystallize via a diffusion-limited process at temperatures

above 120 K, forming polycrystallites through a cylindrical-plate shape. This shape suggests that film thickness is an important factor in determining the crystallization mechanism. The boundary of the polycrystallites is found to crystallize or melt reversibly with decreasing/increasing temperature in the range 80-135 K, much lower than the bulk melting temperature. Analysis of the premelting kinetics allows the determination of the size of the crystallites.

Heterogeneous Nucleation and Wetting of Water Thin Films on a Metal Surface: A Study by Optical Second Harmonic Generation

Through a study of the deposition of water thin films on metal, we have established in Publication 5 that the first step of a molecular film growth process is heterogeneous nucleation of molecular clusters on the surface. A stable layer of critical size nuclei (containing 1-100 molecules) has to be formed within experimental time on the substrate as a template for further film growth.

The condensation of water thin films on a hydrophobic metal surface, Ag(111), was examined using SHG. Condensation coefficient and the fraction of metal surface area covered with water during film deposition were measured in the temperature range of 145-175 K. It was found that under isothermal condensation conditions, the condensation coefficient decreases abruptly to zero at a temperature several degrees lower than that predicted by zero-order desorption kinetics. This catastrophic failure in water film deposition at these temperatures can be explained by the occurrence of wetting-dewetting transition as a result of 3-dimensional cluster formation. Model calculations based on classical nucleation theory, which depicts that heterogeneous nucleation is the initial step of water film deposition, can be used to quantitatively characterize the critical nucleus size as about 100 and the nucleation rate to be slower than 10^{-3} ML-sec⁻¹ at these temperatures.

Determination of Molecular Ordering at a Buried Interface and the Effect of Interfacial Ordering on Thin Film Crystallization by Second Harmonic Generation

In the study of thin films on solid surfaces, it is intuitively expected that the substrate surface structure affects the growth of the films. On a highly corrugated surface, the interfacial layer, i.e. the layer of molecules at the bottom of the thin film, may assume a transitional structure in between the surface and the bulk molecular solid. What would be the structure of

this interfacial layer? How would it be influenced by the substrate surface? Does the interfacial layer structure have any bearing on the continual growth of the film?

It is demonstrated in Publication 7 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. The pyridine molecules in the interfacial layer underneath the film are found to align along the $[\bar{1}10]$ direction of the Ag(110) surface with a small tilt angle ($\sim 11^\circ$) from the surface norm. This interfacial ordering is found to have a notable effect in inducing crystallization at the heterogeneous boundary of the amorphous molecular film.

Adsorption Structure, Energetics, and Thermal and Photochemical Reactions of Vinyl Chloride Monolayer on Ag(111)

With the intention to understand photochemical reactivity of small organic molecules, we have, as the first step, studied the adsorption and thermal reactions of vinyl chloride on Ag(111). Publication 2 showed that vinyl chloride is weakly adsorbed with the molecular plane approximately parallel to the Ag(111) surface plane. The monolayer desorbs molecularly at 119 K in a first order process with desorption activation energy of 6.7 kcal/mol and prefactor of $4.6 \times 10^{11} \text{ sec}^{-1}$. The first few multilayers above the monolayer desorb molecularly at 92 K with an activation energy of 4.3 kcal/mol. At low vinyl chloride coverages, as the Ag(111) surface is heated to greater than 126 K, a small portion ($< 20\%$) of the adsorbed vinyl chloride dissociates with an estimated activation energy of 8 kcal/mole, into vinyl and Cl, which adsorb on Ag(111). Further heating to temperatures greater than 155 K results in vinyl and Cl recombination with subsequent molecular desorption in a second order process with desorption activation energy of 10.7 kcal/mol and prefactor of $2.3 \times 10^{-3} \text{ cm}^2/\text{molecule-sec}$.

Following pulsed 266 and 355 nm ultraviolet laser irradiation, monolayer vinyl chloride on Ag(111) dissociates to C_2H_3 and Cl. Isotopic and energetic effects indicate that the dissociation is through a substrate mediated, electron attachment mechanism. Chemisorbed Cl on the Ag(111) surface inhibits the photodissociation process by increasing the system work function and thereby increasing the minimum substrate electron energy threshold for attachment. Upon heating the Ag(111) substrate, adsorbed vinyl combines to produce 1,3-butadiene in a first order process with an activation energy of 10.4 kcal/mol.

IV. Publications acknowledging this AFOSR grant

A. Published papers

1. Layer by Layer Structure in Ultrathin Films of Aniline and Pyridine on Ag(111)
J. Phys. Chem., 105, 11945 (2001) [letter]; M. C. Yang, T. J. Rockey, D. Pursell and H. L. Dai
2. Adsorption Structure, Energetics, and Thermal Reactions of Vinyl Chloride on Ag(111)
Surf. Sci., 522, 90-104(2003); D. P. Pursell, M-L. Bocquet, J. M. Vohs, and H. L. Dai
3. Surface State Relaxation Dynamics on Ag(110) Probed by Temperature Dependent, Resonantly Enhanced Second Harmonic Generation
Phys. Rev. B, 67, 205410-7 (2003); Susan M. Dounce, Minchul Yang and Hai-Lung Dai
4. Heterogeneous Nucleation and Wetting of Water Thin Films on a Metal Surface: A Study by Optical Second Harmonic Generation
J. Chem. Phys., 118, 5106-5114 (2003); Minchul Yang and Hai-Lung Dai
5. Crystallization and premelting in thin films of weakly interacting molecules: A study of pyridine films on Ag by optical second harmonic generation
J. Phys. Chem. B, 107, 12233-8 (2003), Minchul Yang and Hai-Lung Dai
6. Nonlinear Optical Probe of Structure and Phase Transitions in Ultrathin Molecular Films
SPIE Proceeding on Physical Chemistry of Interfaces and Nanomaterials,(Int. Opt. Soc. Eng. Bellington, WA 2003); Vol. 5223, pp. 49-54, MC Yang, S. Dounce, S. Jen and H. L. Dai
7. Determination of Molecular Ordering at a Buried Interface and the Effect of Interfacial Ordering on Thin Film Crystallization by Second Harmonic Generation
Langmuir [communication], 20, 37-40 (2004), Minchul Yang and Hai-Lung Dai
8. Physisorption on a Metal Surface Probed by Surface State Resonant Second Harmonic Generation
Surf. Sci., in press (2004), Susan M. Dounce, Minchul Yang, and Hai-Lung Dai

B. Student Thesis

Minchul Yang, PhD Thesis, "Structure, Phase Transition, and Nonlinear Optical Properties of Ultra-Thin Molecular Films", University of Pennsylvania, 2002