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Experiments designed to assess the utility of several methods of surface analysis under reaction conditions are described. The goal of the research was to develop new methods with which to understand the mechanisms associated with the preparation of materials of electronic interest by chemical vapor deposition, with an emphasis on laser control of the reactions. The focus of the work was to improve the sensitivity of unenhanced surface Raman spectroscopy through the combined use of ultraviolet lasers, Cassegrain optical systems and charge-coupled device detectors. Model systems to test these technical improvements were designed and an understanding of the factors that govern sensitivity has been achieved. Construction of a system for laser direct writing as well as the installation of a multi-purpose surface analysis system are also described.

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Experiments designed to assess the utility of several methods of surface analysis under reaction conditions are described. The goal of the research was to develop new methods with which to understand the mechanisms associated with the preparation of materials of electronic interest by chemical vapor deposition, with an emphasis on laser control of the reactions. The focus of the work was to improve the sensitivity of unenhanced surface Raman spectroscopy through the combined use of ultraviolet lasers, Cassegrain optical systems and charge-coupled device detectors. Model systems to test these technical improvements were designed and an understanding of the factors that govern sensitivity has been achieved. Construction of a system for laser direct writing as well as the installation of a multipurpose surface analysis system are also described.

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Final Technical Report
AFOSR - 86-0094

**In-Situ Surface Analysis During Laser-Controlled Chemical
Processing of Surfaces**

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20 June 1988

Abstract

Experiments designed to assess the utility of several methods of surface analysis under reaction conditions are described. The goal of the research was to develop new methods with which to understand the mechanisms associated with the preparation of materials of electronic interest by chemical vapor deposition, with an emphasis on laser control of the reactions. The focus of the work was to improve the sensitivity of unenhanced surface Raman spectroscopy through the combined use of ultraviolet lasers, Cassegrain optical systems and charge-coupled device detectors. Model systems to test these technical improvements were designed and an understanding of the factors that govern sensitivity has been achieved. Construction of a system for laser direct writing as well as the installation of a multipurpose surface analysis system are also described.

Introduction

The goals of this research program of limited duration and support were to establish the utility of several experimental methods for the analysis of surfaces undergoing reaction to produce materials of electronic interest. We hoped that the successful results obtained from this feasibility study would support a regular program of work designed to elucidate the molecular level details of such processes as chemical vapor deposition and etching, particularly under laser control, for the production of small (micron) features. In particular, the work focussed upon improving the sensitivity of unenhanced surface Raman spectroscopy (in which this lab is the world leader) to be able to study the very small surface coverages of reactive intermediates present during these surface-mediated reactions. The advantages of surface Raman spectroscopy as a spectroscopic probe include its high molecular specificity, and the ability to operate in nonvacuum ambients. Furthermore, as a scattering spectroscopy, specular surfaces, as for reflection spectroscopy, are not required. Thus, the proposed research was directed toward improving the sensitivity of the Raman technique by 1) employing Cassegrain optics, 2) using ultraviolet lasers as excitation sources, 3) using charge-coupled device detectors. We also proposed to investigate the use of secondary ion mass spectrometry (SIMS) in these studies and explored the practical aspects of laser direct-writing.

Results and Discussion

We approached this problem by designing a test system that would emulate the actual experimental situation in surface Raman spectroscopy. Because of the highly anisotropic nature of the radiation scattered by a molecule near a conducting surface, simple liquid or solid samples would not accurately test new optical layouts. Actually using a molecule adsorbed on a surface in an ultrahigh vacuum chamber would severely restrict our flexibility in optical design. Therefore, we felt it important to design a rugged and reproducible sample that would mimic the intensity and angular distribution of the surface scattering.

We worked through several types of samples. Silicon surfaces were covalently modified with diphenyl methyl silane, diphenyl diethoxy silane and phenyl dimethyl ethoxysilane. Silicon has the advantage in studies like these that the substrate phonons can be used to align the optics rapidly; unfortunately the low number density of surface

CH groups rendered detection so difficult that it would have been all but impossible to make quantitative comparisons as we tested various components.

The most successful system for our work has been a Langmuir-Blodgett film of cadmium arachidate which we could easily obtain spectra from three, five and seven layer films. The advantage of this system is that it is rugged and stable in air. Furthermore, even for a few multilayers, the adsorbate layer is optically thin and the same dipole emission pattern as from a monolayer is seen, thus providing a good model. The first thing that we tested was how much of an improvement a reflective (Cassegrain) optical system would make in throughput. The system (Applied Photophysics) is quoted as an effective $f/0.5$, which would collect four times as much light as our $f/1$ camera lens. The central obscuration of a Cassegrain configuration is of absolutely no consequence in our application since there is a node in the radiation pattern along the surface normal. In addition, since the Cassegrain is a reflective system, it is ideally suited for ultraviolet operation, operating below the glass cutoff and being inherently achromatic. Unfortunately, the improvements we had hoped for didn't materialize; the f -number of the Cassegrain was quoted at infinite conjugation and at the finite conjugation of our experiment the advantage is lost. This, while disappointing, is not a fundamental problem. We simply need to design a custom Cassegrain for our experiment; we are convinced it will bring us the much-needed factor of four.

The second part of our program was to try ultraviolet excitation to increase the Raman scattered intensity. For a vibrational frequency shift of 3000 cm^{-1} one expects a factor of nearly ten increase in the scattered intensity upon going from the 515 nm to the 351 nm argon line, due to the ω^4 dependence of Raman scattering on frequency. We chose a seven layer Langmuir-Blodgett film on silicon as our test system to verify this increase and to gain experience with the ultraviolet optics. We compared spectra taken with 85 mw of 363.8 nm radiation with those taken from 600 mw of 514.5 radiation and the results are shown in Figure 1. Although we clearly have the ability to work in the ultraviolet, there appears to be no advantage to it. This is completely surprising in view of the discussion above and the fact that scattering from the silicon substrate is suppressed at that wavelength. A clue as to what is happening is given by the count rates in the figure. We are not scaling to ω^4 ; our best guess is that some combination of poor optical alignment (ultraviolet lasers

will require some getting used to) and sample degradation under the laser beam are responsible.

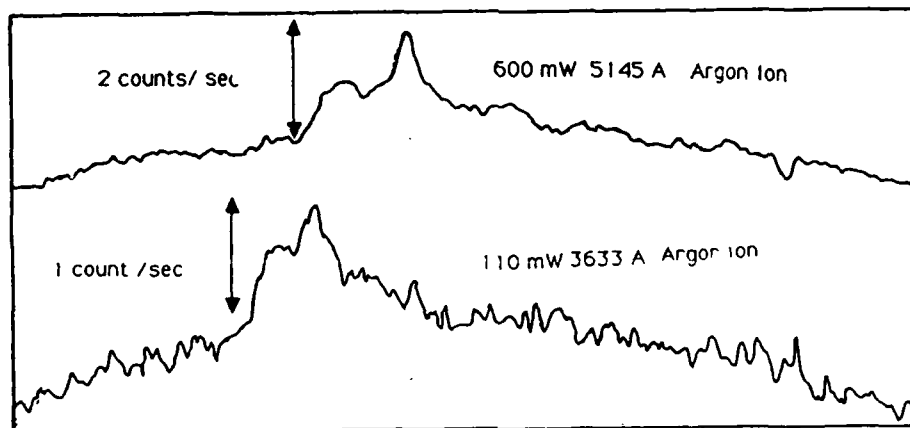


Figure 1

Finally we discuss our evaluation of a cooled charge-coupled device detector to replace our intensified photodiode array. After many years of experience we have finally concluded that, as long as the detector noise characteristics are reasonable, quantum yield is the measure of performance for Raman spectroscopy of condensed phases. This arises because the spectra are always background-noise limited, from some weak underlying continuum, and thus signal-to-noise ratios depend only upon detector quantum yield. Charge-coupled devices become the detectors of choice for this application, then, with quantum yields approaching 0.8, in contrast to 0.1 for an intensified photodiode array. Additionally, CCDs are physically larger allowing integration along the slit direction which reduces power density. Thus, for a given power density, the sample power can be raised by a factor equal to this height increase (approximately four) for an additional improvement in signal-to-noise. We evaluated a Photometrics CCD camera using one of our LB films on silicon as a sample. The particular device had only a 0.4 quantum yield but we easily verified the expected improvement in signal-to-noise. Stretching the beam in the vertical direction also proved useful in allowing us to go to higher powers. Thus the CCD offers a real improvement in sensitivity, one which may make surface Raman

spectroscopy the surface vibrational spectroscopy of choice in the near future.

Summarizing the main accomplishments of this research program, we have investigated systematically the factors required to make unenhanced surface Raman spectroscopy more sensitive. Although the present generation Cassegrain system offers no advantage over transmissive optics, one specially designed for the surface experiment should provide a factor of four improvement. We are similarly optimistic that ultraviolet excitation, when under control, will yield at least a factor of five improvement and the combination of the high quantum efficiency and larger resolution elements of CCDs will add another factor of twenty. Thus a total improvement in sensitivity of a factor of four hundred or an improvement in signal-to-noise of a factor of twenty seems within our grasp. More experience than was provided by this twenty-four month grant will be required to realize these improvements.

Finally we comment on two other areas which received some development during this proposal period. An apparatus for laser decomposition of organometallic precursors to electronic materials has been constructed and tested. A motorized, translating high vacuum chamber is positioned near the focus of a long working length reflecting microscope objective with a diffraction limited focus of $< 3\mu\text{m}$. Decomposition of these precursors and analysis of the features written have been accomplished using scanning electron microscopy and energy dispersive X-ray analysis. In the second area, our multipurpose ultrahigh vacuum surface analysis chamber has finally been delivered and installed. After more than a usual amount of difficulty with manufacturing and installation problems, we now have X-ray photoelectron spectroscopy, ion scattering spectroscopy, secondary ion mass spectrometry and Auger electron spectroscopy in an instrument with both high and low pressure sample preparation chambers. Part of this instrument was purchased under the DoD-URIP with support from ASOSR. Thus the laboratory is now exceptionally well-equipped to handle research into the microscopies of surface-mediated reactions related to electronic materials preparation.