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Reactions of laser-generated free radicals at semiconductor surfaces have been investigated by photoelectron spectroscopy of adsorbed surface layers and by laser-induced fluorescence detection of the gas-phase species. Systems investigated include dissociative chemisorption of XeF_2 and CF_3 on Si(111), IR multiple-photon dissociation of alkylsilanes and characterization of the SiH_2 dissociation product and deposition of metallic films from iron carbonyl. From these experiments, quantitative models have been developed for the reactivity of fluorocarbon radicals at silicon surfaces, intersystem state coupling in excited SiH_2, and formation of metallic films.

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FINAL REPORT

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"Reactions of Laser-Generated Free Radicals
at Semiconductor Surfaces"

by

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(22 January 1990)

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Introduction

The reactions of neutral fluorocarbon free radicals at silicon-containing surfaces are an important component of the mechanism of reactive etching of such surfaces during the production of microelectronic devices; however, isolating such reactions in a plasma environment is difficult or impossible, because of the simultaneous presence of other reactive species such as energetic ions and electrons. For this reason, we have used photolytic methods for selective generation of such radicals and subsequent investigation of their reactions with semiconductor surfaces, such as silicon and silicon oxides.

Reactions of Laser-Generated Fluorocarbon Radicals at Silicon-containing Surfaces.

The radicals CF_3 and CF_2 have been produced by infrared multiphoton dissociation (IRMPD) or u.v. photodissociation, respectively, of perfluorinated precursor species, and the overlayers resulting from reaction of these radicals with adjacent silicon-containing surfaces have been examined by X-ray Photoelectron Spectroscopy. Auger Electron Spectroscopy, and Thermal Desorption Spectrometry [11, 15, 16, and 17]*. On the basis of these results, and complementary experiments using molecular fluorinating agents such as XeF_2 [4, 10] and NF_3 [18,19], we have proposed a simple theoretical model based on the strengths of chemical bonds made and broken at the reacting surface, which appears to account satisfactorily for most of the observed behavior [16,18]. The CF_3 radical can bind to dangling bonds on the Si(111) or Si(100) surface, but does not do so readily on the SiO_2 surface because breaking the surface Si-O bond requires more energy than is returned by forming a Si–C bond. The SiO_2 surface must first be disrupted e.g., by argon-ion bombardment, to create binding sites for CF_3. On a Si surface, a bound CF_3 will transfer at least some of its fluorine atoms because of the greater binding energy of Si-F vs. C-F. On a SiO_2 surface, such transfer is inhibited because both a C-F and a Si-O bond must be broken in order to produce the Si-F bond. CF_2 appears to bind more readily to SiO_2 than does CF_3; this can be understood on the basis of the divalent carbon producing a new Si-C and a C-O bond, which compensates for the energy required in the Si-O bond breaking step. In the case of valence-saturated species, such as XeF_2 on SiO_2, there appears to be a substantial barrier to dissociative chemisorption.

Related experiments were also carried out to characterize the IRMPD process utilized for production of CF_3 radicals [3, 5], and the product-state distribution and surface loss coefficient of CF_2 radicals produced by u.v. photodissociation of C_2F_4 [6, 21].

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* Numbers in brackets refer to the list of publications which follows.

Laser-Initiated Chemical Vapor Deposition

Laser-initiated dissociation of gas-phase precursors can also lead to deposition of thin films, e.g. of amorphous silicon [7, 20] or metallic materials. In the IRMPD of organosilanes and silicon hydrides, silylene has been postulated as a key intermediate leading to deposition of silicon films. The SiH_2 fragment so produced has been detected by laser-induced fluorescence (LIF) [1]. A remarkable variation in the fluorescence lifetimes of individual rovibronic levels of the $\tilde{A}^1B_1$ state of SiH_2 is observed, with decay rates varying by over two orders of magnitude between neighboring transitions [8]. This variation is attributed to mixing of the $\tilde{A}$ state with high vibrational levels of the $\tilde{X}^1A_1$ state and/or nearby triplet states, such as the $\tilde{a}^3B_1$ or the $^3A_2$, and with the dissociative continuum of $Si(^3P)+H_2$. The distribution of lifetimes has been examined from an information-theoretic point of view, in collaboration with Professor R.D. Levine and his co-workers at the Hebrew University [9, 14]. The measured distribution is well fitted by a maximal-entropy expression for the decay rates, which in turn implies that the level spacings distribution at ca. 18,000 cm^{-1} total energy in the neighboring triplet and $\tilde{X}^1A$ states is chaotic and uniformly samples its available phase space.

By extending the LIF measurements to higher vibrational levels in the $(0v_20)$manifold, including the region at which calculations by Francisco and co-workers indicate that the $Si(^1D_2)$ dissociation channel becomes available [12], we are able to establish the location of the $Si(^1D_2) + H_2$ dissociation channel. Its position, between $v_2'=6$ and 7, allows us to determine the standard heat of formation of $SiH_2(g)$ as $\Delta H_f^o = (65.4 \pm 1.6)$ kcal $mole^{-1}$. [13].

Experiments have also been undertaken to characterize the processes occurring in deposition of metallic films from u.v. photolysis of metal carbonyls such as $Fe(CO)_5$. From XPS and Auger analysis of the deposited films, and measurements of their growth rate, we have developed a model which includes both gas-phase initiation and subsequent dissociation (thermally and/or photochemically driven) of the photodeposited material [22].

Although a satisfying portion of the work originally proposed was accomplished during this research program, with a number of significant findin[illegible]orted in the process, there still remain many further important unresolved questions concer[illegible]e dynamics of laser-initiated gas-surface reactions. It is clear, for example, that the thermochemical model developed for radical -surface reactions [16] cannot account satisfactorily for reactions in which there is a substantial energy barrier in the dissociative chemisorption channel. More accurate ab initio or semi-empirical models of adsorbate-surface interaction energies are now beginning to appear, and should be applied to the systems we have studied. There are also intriguing suggestions, both in our work [6, 20] and results from other laboratories, that the reactivity of radicals at surfaces depends strongly on their vibrational energy content. State-resolved optical

diagnostics, such as LIF and REMPI, afford the possibility of investigating such dependences. Finally, our results on photodeposition of metallic films from carbonyls [22] suggests the possibility of photodissociation processes occurring in the freshly deposited materials which differ substantially from analogous gas-phase processes. All of these questions have interesting implications for molecular dynamics, as well as addressing practical issues of improved efficiency and control for photon-driven processes in microelectronic device fabrication. It is thus regrettable that this research program has not been continued.

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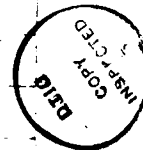

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