Chem. Rev. 1989, 89, 1291-1301

Reactions of Photogenerated Free Radicals at Surfaces of Electronic Materials

JEFFREY I. STEINFELD

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received August 31, 1988 (Revised Manuscript Received January 3, 1989)

Contents

I. Introduction

Ever since the formation of molecular free radicals in the gas phase was demonstrated by Paneth,[1] Rice,[2] and co-workers, the interaction of such species with surfaces has been a matter of concern to chemists. The customary situation is that such interaction has a deleterious effect, since free radicals tend to recombine or are otherwise deactivated on surfaces, thus decreasing their availability for participation in other chemistry. The increasing importance of plasma-assisted chemical etching (PACE) and chemical vapor deposition (PACVD), especially in the fabrication of microelectronic devices, has made it necessary to understand in detail the chemical reactions that ensue when free-radical species impinge on surfaces, since free radicals are an important constituent of such plasmas.

Jeffrey I. Steinfeld is Professor of Chemistry at the Massachusetts Institute of Technology. He received the B.S. degree from M.I.T. in 1962 and the Ph.D. degree from Harvard University in 1965 and was a National Science Foundation Postdoctoral Fellow with Prof. Sir George Porter at the University of Sheffield (U.K.). He has authored books on the subjects molecular spectroscopy (*Molecules and Radiation*, M.I.T. Press) and chemical kinetics (*Chemical Kinetics and Dynamics*, with J. S. Francisco and W. L. Hase, Prentice-Hall). He is a coeditor of *Spectrochimica Acta*, *Part A*.

The subject of this review is the reactions of photogenerated free radicals at the surfaces of electronic materials. Some definitions are in order at the outset. The most appropriate definition of a free radical for our purposes is a *reactive valence-unsaturated species*, that is, a "transient species...that has a short lifetime in the gaseous phase under ordinary laboratory conditions".[3] A somewhat more colorful definition is that of "a chemical reaction waiting to happen".[4] These definitions encompass that of the traditional free radical possessing one or more unpaired electron spins, such as CF_3 and NF_2; species in which the ground electronic state is an electron-paired singlet but which are nevertheless highly reactive, such as CF_2 and SiH_2; and atomic species such as F and Cl. By "photogenerated", I include any process that relies on a photolysis source for free-radical production: this includes UV photodissociation with broad-band sources or with excimer, N_2, or frequency-doubled argon ion lasers; or infrared multiple-phonon dissociation (IRMPD), typically using a high-intensity pulsed CO_2 laser. Finally, by "electronic materials" I mean any substrate that is commonly used in microelectronic device manufacturing. This includes semiconductors, primarily silicon (single crystal or polycrystalline) and gallium arsenide;

0009-2665/89/0789-1291$06.50/0

insulators such as silicon oxide or silicon nitride; and conducting metals used for interconnects, such as Al, Au, Cd, Cu, Mo, Ni, or W, and alloys of these species. To this list could be added the copper oxide based superconducting materials, for which a number of laser processing techniques are currently under development, but investigations of these systems are too recent to be appropriate for a review, and there is no suggestion thus far that free-radical chemistry plays a role in laser deposition of high-T_c superconductors.

The scope of this review is intentionally limited to a discussion of the surface reaction chemistry of those free-radical species that are important in the processing of electronic materials. The emphasis is on the uses of photoinitiation as a clean, well-characterized source of specific free radicals, free of the complications (ions, electrons, other reactive species) present in a plasma; in this way, the surface chemistry of a specific free-radical species may be unambiguously characterized. Device and materials aspects have been extensively reviewed elsewhere[5] and will not be discussed in detail here. The basic mechanisms of laser etching and deposition have been reviewed by Houle,[6] with numerous examples (126 references). In addition, numerous reviews have appeared that deal with the photolysis processes themselves, such as IRMPD,[7-9] so this topic will not be covered in detail. In the body of this review, the following topics will be specifically considered: photogeneration of reactive species by infrared or UV photolysis; experimental methods for coupling photoinitiation and surface-analysis techniques; results for specific systems; and a simple bond-energy model for reactions taking place at the surfaces of silicon-containing materials.

II. Photogeneration of Reactive Species

In this section, we consider the various photolysis techniques that have been used to produce the free-radical species that have been most thoroughly investigated in the present context: fluorocarbons (CF_3 and CF_2), nitrogen fluorides, and silicon hydrides (SiH_3 and SiH_2). The surface reactions resulting from these species will be discussed in section IV.

A. Trifluoromethyl

Since the CF_3 radical is one of the principal components of fluorocarbon etching plasmas,[10] studying the reactions of this species with silicon surfaces is a matter of great interest. As with most saturated carbon systems, the electronic absorption of CF_3X (X = halogen, hydrogen, or alkyl) lies in the deep ultraviolet. Washida and co-workers[11] photolyzed CF_3H, CF_3Br, and CF_3Cl using various atomic resonance lines between 100 and 130 nm; Quick et al.[12] used VUV synchrotron radiation to photolyze CF_3Cl, CF_3Br, and CF_3I between 110 and 135 nm; and Dreyfus and Urbach[13] used frequency-tripled dye laser radiation to photolyze CF_3Br at 121 nm. In all these cases, electronically excited CF_3^* was observed as a product. CF_3Br does possess a weak absorption at the ArF excimer laser 193-nm wavelength; this has been utilized by Brewer et al.[14] and Armacost et al.[15] in their studies of CF_3 interactions with GaAs and polysilicon, respectively.

Decomposition of CF_3-containing molecules by IRMPD[7-9] is a facile process, since the C–F bond is an effective "infrared chromophore", resonantly tuned to the output frequencies of the 9-μm band of the CO_2 laser. Suitable precursor molecules include CF_3I,[16,17] CF_3Br,[18] and CF_3Cl.[19] CF_3 may also be produced by IRMPD of hexafluoroacetone, with CO as a byproduct.[20,21] CF_3I has been used as a CF_3 source by Selamoglu et al. in their study of reactions at fused-silica surfaces[22] and by Robertson et al. in the continuation of those studies;[23,24] $(CF_3)_2CO$ was also used in the latter work. CF_3Br was used as the CF_3 source in the first reported studies of photogenerated free-radical reactions on silicon-containing surfaces.[25]

One possible difficulty with the foregoing CF_3 precursors is that potentially reactive byproducts, such as halogen atoms or CO molecules, are produced in the photolysis step. This difficulty is not encountered when C_2F_6 is used as a precursor. This species is efficiently dissociated by the 9R(30) CO_2 laser line, at moderate fluences (5–6 J cm^{-2}).[26-28] C_2F_6 was used as the CF_3 source in the experiments of Roop et al.[29] and Joyce et al.[30]

One possible complication arising from the use of IRMPD to generate CF_3 radicals from CF_3X is secondary dissociation of CF_3 to CF_2 + F. The production of CF_2 from IRMPD of CF_3Br was observed by Würzberg et al.[31] and attributed to secondary dissociation of CF_3. However, Sudbo et al.[32] observed no "significant" secondary dissociation in the molecular beam–IRMPD studies of CF_3X (X = Cl, Br, I). Thoman[33] studied secondary dissociation yields in IRMPD of CF_3Br, CF_3I, and C_2F_6 with laser-induced fluorescence (LIF) detection of CF_2 and compared the observed signals to those obtained in the IRMPD of CF_2HCl. He concluded that at most a few percent of the CF_3 radicals produced by IRMPD may undergo secondary dissociation to CF_2 + F, and this can be minimized by operating at a CO_2 laser fluence just above the dissociation threshold.

B. Difluorocarbene

While CF_2 is readily produced by IRMPD of CF_2HCl[34] or CDF_3,[35,36] the resulting hydrogen halide byproduct is likely to interfere seriously with ensuing reactions on silicon-containing surfaces. UV photolysis has been the more common route to this species. Photodissociation of CF_2Br_2 at 248 nm (KrF excimer laser) yields CF_2Br + Br;[37] the former may undergo secondary photolysis at this wavelength to yield CF_2 + Br. Excimer laser photolysis of CF_2Br_2, at 248 and 193 nm,[38] was used by Brannon[39] in his study of photochemical etching of silica glass. A two-photon mechanism is also invoked by Loper and Tabat[40] in their use of KrF laser photolysis of CF_2Cl_2 for etching silicon oxide.

A clean source of CF_2 with no reactive byproducts is UV laser photolysis of C_2F_4. The quantum yield for dissociation to $2CF_2$ is 1.0 between 185 and 209 nm,[41] and production of CF_2 is efficient with the ArF excimer laser at 193 nm.[33] This source has been used by Langan et al.[42] in their study of CF_2 reactions with silicon and silicon oxide surfaces.

C. Nitrogen Fluorides

NF_3 has been proposed as a plasma etchant,[43] since it produces etch rates greater than those of halocarbon plasmas, shows greater selectivity, and is claimed to leave only volatile species as byproducts, thereby eliminating etch-blocking deposition of polymer. The parent NF_3 is reported[49] not to etch either Si or SiO_2.

NF_3 can be dissociated to NF_2 + F by either the ArF excimer laser 193-nm line[15,45,46] or (via IRMPD)[47] by CO_2 laser 10-μm P-branch lines between 922 and 944 cm^{-1}. Etching of silicon has been reported under these conditions,[15,45-47] but the reactions are most likely due to the fluorine atoms liberated in the photolysis. N_2F_4 can be readily dissociated into two NF_2 radicals by expansion into a heated oven,[48] but N_2F_4 is a hazardous material and must be handled with extreme caution.[49]

D. Silicon Hydrides

Silyl (SiH_3) and silylene (SiH_2) radicals are implicated in the chemical vapor deposition of silicon thin films.[50] However, direct production of these radicals is not straightforward. IRMPD of silane[51] leads to $SiH_2 + H_2$, but the CO_2 laser lines are somewhat off-resonant from silane absorption features,[52] so that IRMPD must be either collision-assisted or result from dielectric breakdown at high pulse intensities. IRMPD of organosilanes[53] does not lead to rupture of the C–Si bond, but rather elimination of SiH_2; this has been verified by LIF detection of the resulting silylene.[54-57] In fact, the silylene has been shown[58] to be a secondary dissociation product arising from an RSiH (R = alkyl) fragment, resulting from an initial H_2 elimination step. It may also be noted that SiH_2 itself dissociates to Si atoms and H_2 following electronic excitation to the $\tilde{A}^1B_1$ state.[57,59,60]

Few direct routes to SiH_3 radical are reported in the literature. Mercury sensitization is reported[61] to initiate Si–H bond breakage

$$Hg(^3P_1) + SiH_4 \rightarrow Hg(^1S_0) + H + SiH_3 \qquad (1)$$

and hydrogen atoms are said to be quantitatively converted to silyl in low-power discharges in silane[62] by the abstraction reaction

$$H + SiH_4 \rightarrow H_2 + SiH_3 \qquad (2)$$

E. Photogenerated Atomic Free Radicals

Photolytic generation of atomic free radicals is a well-established technique in chemical kinetics, which has been used to study surface reactions of atoms on a number of occasions. The UV photolysis and IRMPD of NF_3 produces F atoms in addition to the NF_2 radical (section II.C), and these atoms may be primarily responsible for the ensuing surface chemistry. Carbonyl difluoride may also be photolyzed at 193 nm (ArF excimer laser) to yield F atoms,[63,64] and Br atoms generated by 193-nm photolysis of HBr have been found to etch GaAs.[65] Molecular chlorine may be photolyzed at a variety of wavelengths, including 248 (KrF excimer), 308 (XeCl excimer), 337 (N_2 laser), 423 and 532 nm (frequency-doubled Nd:YAG), and 583 nm. The chlorine atoms so generated are found to etch silicon and copper surfaces.[66-68] Rothschild and co-workers[69] have also found that Cr, Mo, and W films are etched by Cl_2 when exposed to 488-nm radiation from an argon ion laser. In this case, as well as others in which longer wavelength visible radiation is employed,[67,68a] photodissociation of Cl_2 adsorbed on the metallic surface must play an important role in the process.

Numerous instances of metallic film deposition following photodissociation of volatile metal–organic compounds have been reported. Among the species so deposited are the elemental species Al, Au, Cd, Cr, Cu, Fe, In, Ir, Mn, Mo, Ni, Pt, Sn, Ti, W, and Zn and alloys including Al_xTi_y, GaAs, $Hg_{1-x}TeCd_x$, and InP. A fairly complete bibliography is given in ref 5. The UV-photoassisted growth of II–VI compounds, such as $Hg_{1-x}TeCd_x$ has been reviewed in detail by Irvine.[70a] Since chemical vapor deposition is the subject of other articles in this thematic issue, this topic will not be extensively discussed here.

In most cases, the photodeposited materials have the form of metallic films or stoichiometric alloys. This would appear to suggest that the photolysis products are primarily atomic metals and that partially dissociated free-radical species are not implicated in the deposition process. The actual situation is frequently more complicated than this, since the primary photolysis step, in many instances, is known to yield metal–organic radicals. For example, the gas-phase photolysis of $Fe(CO)_5$ at 193 nm yields primarily the $Fe(CO)_2$ photofragment.[70b,c] Analysis of metallic films produced by photolysis of carbonyl precursors (Mo, W, and Cr;[70d] Fe[70e]) shows the presence of carbon and oxygen incorporated in the films, which presumably results from subsequent surface photolysis of adsorbed subcarbonyls.

III. Experimental Methods

A number of methods have been used to interrogate materials following exposure to photogenerated free radicals. A good survey may be found in ref 70f.

A. Diagnostic Techniques

1. Etch Rate and Morphology

The overall rate of etching (removal of material from the surface) or deposition may be determined in several ways. If the etched or deposited features are produced by a focused laser beam imaged on the surface, the height of the feature may be determined directly by scanning-stylus-probe profilometry,[14b,15,25,39,63,65,67] using a Dektak or equivalent instrument. This method fails, however, if the features are too small or too deep. An alternative approach for measuring film thickness is to use an optical probe such as ellipsometry; if the film is reasonably uniform, is not too thick, and is deposited on a transparent substrate, transmittance of an optical probe beam may be used to measure film thickness if the optical constants of the deposited material are known.[69b,71,72] Scanning electron microscopy is frequently used in conjunction with film thickness measurements in order to determine the topography of the etched or deposited features;[14b,15,25,39,40a,53,64,65,69b] the morphology of the deposit may be accessible to transmission electron microscopy.

Instead of profile measurements, the net etching or deposition rate may be determined with a quartz crystal microbalance.[73] The advantage of this technique is that sample mass, and therefore rate of material deposition or removal, may be monitored continuously throughout the irradiation.[47,68a] Such measurements are difficult to carry out quantitatively, however, because of the vibrational and temperature sensitivity of the microbalance.

2. *Surface Composition*

The principal technique that has been used for determining surface compositions following exposure to free radicals is electron spectroscopy, including XPS,[29,30,42,47,68a] X-ray microprobe analysis, and scanning Auger spectroscopy.[53,69c] XPS and/or Auger depth profiling is a valuable adjunct to surface composition measurements, and secondary-ion mass spectrometry (SIMS) is often of use as well. Such measurements are particularly valuable for elucidating the details of the reaction chemistry occurring between the free radical and the surface. While numerous techniques have been developed for optical spectroscopy of surfaces and thin films, such as surface-enhanced Raman spectroscopy,[74,75] attenuated total reflection,[76] and photoacoustic[77-79] or photothermal spectroscopy, these techniques do not yet appear to have been extensively applied to the study of free radical–surface reactions. The use of such optical techniques should play an increasingly important role in the future.

3. *Gas-Phase Composition*

The rate of gas–surface reactions may be inferred by measuring the effect of introduced substrate materials on radical concentrations in the gas phase above the surface. This may be done by using either mass spectrometry or optical measurements. The former approach includes techniques such as very-low-pressure photolysis (VLPΦ), which has been used to study CF_3 reactions on various materials.[22-24] As shown in the following section, however, such measurements require careful interpretation. Time-of-flight mass spectrometry may be used to monitor products of gas–surface reactions following pulsed laser excitation.[66,68b]

Various types of optical spectroscopy may be applicable to monitoring species participating in gas–surface reactions. LIF has been used to measure CF_2 concentration profiles above a silicon surface,[81] thereby determining surface reaction probabilities for this species. Coherent anti-Stokes Raman spectroscopy (CARS) has been used for profiling silane and germane in radiofrequency discharge plasmas.[82a–c] Resonance-enhanced multiphoton ionization (REMPI) has been used to detect both the I and Br atoms[24b] and the CF_3 radicals[82d] formed in the IRMPD of CF_3I or CF_3Br.

B. Considerations in Coupling Photoreaction Chamber to Analysis Chamber

In order to obtain meaningful measurements of surface compositions following dosing with a flux of free radicals, it is essential that the measurements be performed in situ, so that there is no exposure of the material to air or other contaminants between the dosing and the analysis. This requires that the sample be transferred to an ultra-high-vacuum (UHV) analysis chamber immediately following dosing without breaking vacuum integrity. This imposes several constraints on apparatus design, since the conditions required for free-radical generation may not be compatible with UHV requirements. A lengthy exposure to moderately high pressures (milliTorr to several Torr) of radical precursors is often required, and these precursors may be sufficiently reactive or corrosive that their introduction into a UHV chamber containing sensitive components such as electron multipliers would be highly undesirable. In addition, optical ports must be provided for admitting the laser beams used to photolyze the precursors, and the window materials are frequently incompatible with UHV requirements, particularly anti-reflection-coated zinc selenide required for transmitting 10-μm CO_2 laser radiation.

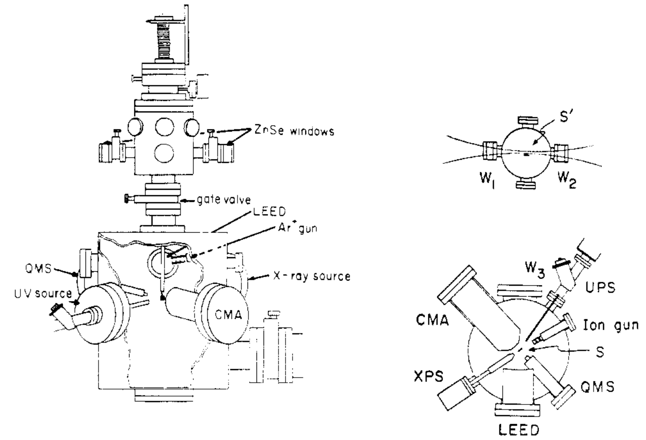


Figure 1. Plan and elevation of two-stage vacuum chamber for surface analysis of materials following free radical reaction (from ref 84). All photolysis and dosing are done in the upper chamber. The lower (UHV) chamber includes a LEED/Auger instrument and ion gun for sputter-cleaning and subsequent examination of the sample; below this is a He resonance lamp, Mg Kα X-ray source, and electron energy analyzer for photoelectron spectroscopy. A Balzers Model 311 quadrupole mass spectrometer is also located in this plane for use in thermal desorption studies. W_1 and W_2 are optical ports for the laser beams, and W_3 is a view port for observing the LEED pattern. S denotes the position of the sample for XPS or TDS measurements; S' denotes the sample position during dosing, using parallel irradiation geometry (see section III.C).

There are two generic approaches to solving this problem. The one we have taken, as illustrated in Figure 1, involves a separate reaction chamber mounted above the UHV analysis chamber. The sample is transported between the two chambers by a long Z-stroke manipulator incorporating a two-stage differentially pumped rotary seal adapted from the design of Auerbach et al.[83] Differentially pumped windows (AR-coated ZnSe for infrared lasers, UV-S grade quartz for excimer lasers) are mounted on the upper reaction chamber. With this apparatus, a sample can be cycled repeatedly between the reaction and analysis chambers to monitor the progress of the surface reactions.[84]

An alternative approach makes use of a vacuum transporter to move the sample between the irradiation and analysis chambers. An advantage of this design is that, with suitable high-vacuum valves, it is possible to transfer the exposed sample to specialized analysis facilities which may be physically remote from the laser irradiation equipment; a drawback is that it is not very convenient to carry out repeated analyses during the course of a reaction. Designs of this type have been described by Helms et al.[85] and by Ninomiya et al.[86]

C. Models for Photoinitiated Surface Reactions

A complete description of the photogeneration and ensuing surface reactions of free radicals involves a large

TABLE I. Summary of Fluorocarbon Reactions on Silicon and Silicon Oxide

substrate	XeF_2 (F simulant)	CF_3 (C_2F_6 IRMPD)	CF_2[a] (C_2F_4 photolysis)
Si(100) 2×1 Si(111) 7×7	amorphous Si:F reactive overlayer formed at high exposures (ref 91)	undergoes dissocative chemisorption (ref 29, 30)	undergoes partial dissociative chemisorption (ref 42)
thermal SiO_2	chemisorption requires lattice damage by ion bombardment (ref 92)	does not dissociate on damaged or undamaged surface (ref 30)	adsorbs but does not dissociate on damaged or undamaged surface (ref 42)

[a] Reaction probabilities measured over Si(100) by LIF profiling.[81]

number of processes, including photodissociation of precursor molecules, both in the gas phase and at the surface; transport of free radicals and of undissociated precursor species, by both molecular flow and diffusion; surface reactions including chemisorption, polymerization, and product desorption; and gas-phase radical reactions, such as recombination. Several approaches have been made to obtain approximate analytic solutions for such systems,[46,72,87,88a–c] which are in reasonable agreement with experimental measurements.

A basic distinction should be made between experiments in which the laser beam is directed perpendicular to and strikes the surface and those in which the beam is directed parallel to and a short distance (a few millimeters) above the surface. In the former case, photodissociation may occur both in the gas-phase column defined by the beam path between the entrance window and the surface and in the adsorbed layer of precursor molecules on the surface. Several authors[87,89a] have shown that the absorption and photofragmentation spectra of molecules can be greatly altered in going from the gas phase to an adsorbed phase; frequently, adsorbed molecules can be dissociated at much longer wavelengths than they can be when in the gas phase. Local heating of the surface at the point of intersection with the laser beam can also play a significant role in the process.[88a,88c]

The situation is considerably simplified if the laser beam is parallel to and does not interact with the surface.[29,30,42] In this case, photodissociation occurs solely in the gas phase, and the surface can be maintained at an independently controlled temperature. This configuration is, in fact, essential when using IRMPD to generate free radicals, since a single pulse from a high-intensity CO_2 laser is sufficient to induce catastrophic damage to most substrates.[89b] Suzuki[81,90] has found an analytic solution for free-radical concentration profiles in the gas phase above a surface, assuming a constant rate of radical production and diffusion-controlled transport to the surface. The expression is

$$\tilde{n}(z) = \frac{n(z)}{n(0)} = \frac{3}{4}(\alpha_r/\lambda_r)z + 1 \qquad (3)$$

where $\tilde{n}$ is the density of radicals at a distance z from the surface, normalized to the density at $z = 0$, λ_r is the mean free path of radicals in the gas, and α_r is the effective removal probability (reactive accommodation coefficient) of the radicals at the surface. The linear dependence of $\tilde{n}(z)$ on z predicted by eq 3 has been verified experimentally[81] for CF_2 radicals over various substrates ($1 < z < 10$ mm), and values of α_r could be obtained from the slope of the linear portion of the $\tilde{n}(z)$ curve. Solutions with a time-dependent radical source, such as pulsed laser photolysis, are more complex.[90]

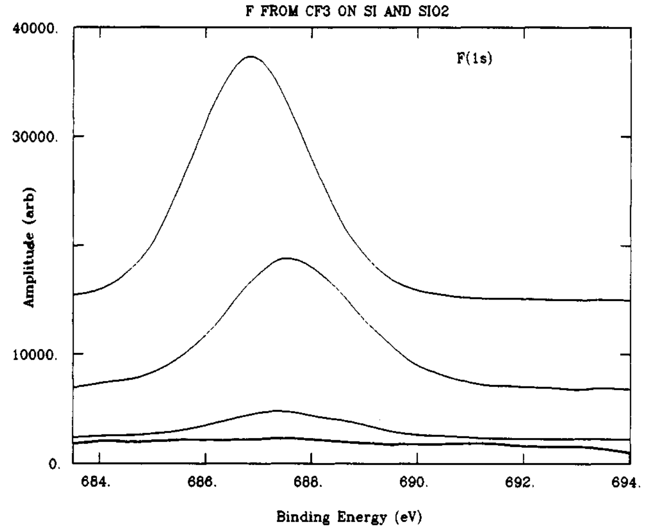


Figure 2. F(1s) core-level spectra from XPS of various silicon and silicon oxide surfaces following adsorption of CF_3 produced by IRMPD of 40 mTorr C_2F_6 with 72 000 pulses of the CO_2 9R(30) laser line at 250 mJ/pulse. From bottom to top: with exposure to C_2F_6, but no laser irradiation; CF_3 on annealed thermally grown silicon oxide; on silicon oxide surface with argon ion presputtering; on Si(100) surface (adapted from ref 30).

IV. Results for Specific Systems

A. Fluorocarbon Radicals on Silicon and Silicon Oxide

The most thoroughly studied set of reactions included in this review is that of CF_3 and CF_2 with silicon and silicon oxide surfaces. The results for these systems, along with base-line studies of XeF_2 on the same substrates[91a–c,92] are summarized in Table I. In these experiments, F(1s) and C(1s) XPS measurements provide most of the quantitative information. Figure 2 shows the F(1s) XP spectra obtained after dosing Si and SiO_2 surfaces with CF_3 derived from IRMPD of C_2F_6. The fluorine coverage on silicon is proportional to CF_3 dose and shows a slow increase at high exposures due to formation of a fluorinated silicon overlayer.[29,91a] Much less fluorine uptake occurs on silicon oxide surfaces, unless the surface is damaged prior to exposure by argon ion sputtering.[30] This behavior exactly parallels that found for XeF_2 on silicon oxide surfaces.[92] It should be noted that C_2F_6 is essentially unreactive with silicon or silicon oxide surfaces, so that the reaction of the CF_3 radical can be readily observed.

From the C(1s) XP spectra shown in Figure 3, we can see that the carbon resulting from CF_3 exposure is bound to the silicon surface in carbidic form, with a nominal core-level energy of 283 eV. This implies that some or all of the fluorines have spontaneously transferred from carbon to silicon atoms. At higher CF_3 doses,[30] or when the surface has been contaminated by

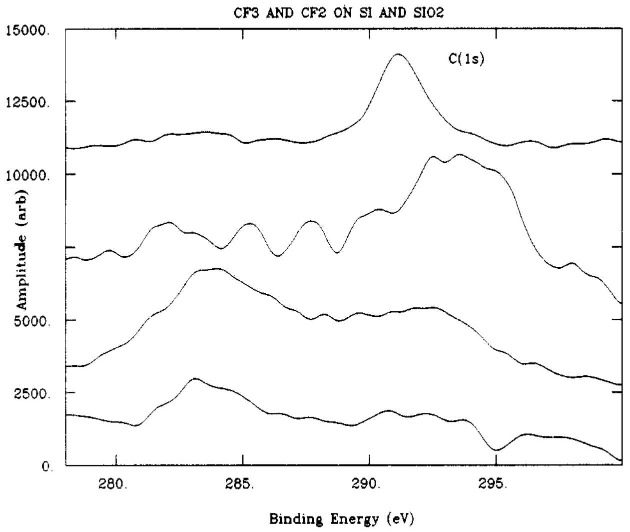


Figure 3. C(1s) core-level spectra from XPS of various silicon and silicon oxide surfaces following adsorption of fluorocarbon. From bottom to top: CF_3 on Si(100) with 72 000 CO_2 laser pulses in 40 mTorr C_2F_6; on Si(100) with 72 000 laser pulses in 400 mTorr C_2F_6; on presputtered SiO_2 with 72 000 laser pulses in 400 mTorr C_2F_6; annealed SiO_2 following exposure to CF_2 from 193-nm irradiation in 40 mTorr C_2F_4. The C(1s) peak near 283 eV is characteristic of carbidic (nonfluorinated) carbon, while the peaks near 291 and 294 eV arise from difluorinated and trifluorinated carbon, respectively (adapted from ref 30 and 42).

adventitious hydrocarbons,[29] the C(1s) intensity at 294 eV grows in, indicating that CF_3 is being adsorbed without undergoing dissociation or fluorine atom transfer. On a silicon oxide surface, only the 294-eV peak appears, indicating that CF_3 is bound to the oxide surface as an undissociated fragment.[30] Preliminary experiments[93] on the interaction of CF_3 with silicon nitride indicate that the nitride behaves similarly to the oxide. CF_2 (from UV photolysis of C_2F_4) binds to silicon oxide more readily than does CF_3, and the position of the C(1s) peak shown in Figure 3 indicates that fluorine transfer from carbon to silicon is not taking place.[42] On silicon surfaces, the C(1s) XP spectra are more complex, indicating that partially dissociative chemisorption of CF_2 is occurring. There is also a background reaction that occurs when silicon surfaces are exposed to C_2F_4 in a metal vacuum system, which complicates the interpretation.

The reaction of CF_3, derived from IRMPD of CF_3I, with silicon and silicon oxide surfaces has also been studied by using the VLPΦ technique. Initial observations[22] that appeared to indicate reaction of CF_3 with the oxide surface were later reinterpreted[23] as resulting from reactions with stainless steel components in the apparatus. This illustrates poignantly the need for careful surface characterization in such measurements. In subsequent experiments,[24a] the reaction of CF_3, derived from IRMPD of either CF_3I or hexafluoroacetone, with silicon wafers was examined. The reaction probability ϵ_r as determined from the ratio of SiF_4 product flux to CF_3 radical density, was determined to be between 10^{-4} and 10^{-5} at substrate temperatures of 560–745 K. This is comparable with the value for molecular (not atomic) fluorine at somewhat lower temperatures.[94] Inhibition by adsorbed carbon was also noted, in agreement with the findings of Roop et al.[29]

Among other investigations of CF_3–semiconductor interactions, we may note those of McFeely et al.,[95] who investigated the spontaneous reaction of $(CF_3)_2N_2$ with silicon and silicon oxide surfaces. The reaction with silicon leads to a complex set of products, including nitrogen incorporation at the surface. The results do show, however, that transfer of fluorine atoms from carbon to silicon proceeds without a significant activation barrier and that carbon contamination passivates the surface to further reaction, in agreement with the previous studies. In the case of SiO_2, lengthy UV exposure and enormous $(CF_3)_2N_2$ doses were required to obtain observable uptake of carbon or fluorine on the surface. Etching of GaAs by UV-photolyzed CF_3Br has been reported,[14] but the surface compositions were not characterized in detail. The structure of CF_3 on GaAs, following exposure to a CF_4 plasma, has been studied by RHEED and photoelectron spectroscopy.[96]

As noted above, photogenerated CF_2 binds to silicon and silicon oxide surfaces but does not undergo dissociation on the oxide.[42] This is in apparent disagreement with the results of Brannon[39] and Loper and Tabat,[40] who reported "efficient" etching of oxide surfaces exposed to excimer laser radiation in the presence of CF_2 sources such as CF_2Br_2, CF_2Cl_2, or C_2F_4. It must be remembered, though, that in the etching experiments the surface is directly irradiated by high-intensity UV light, which could lead to processes such as photon-stimulated desorption, thermal and/or electronic excitation of the surface, or release of fluorine atoms by "surface-catalyzed" secondary photodissociation. The measurements of Thoman et al.[81] on CF_2–surface reaction probability, using LIF profiling, should also be mentioned in this context. Surface loss probabilities (α_r) between 0.01 and 0.03 were found over Si(100), and about a factor of 3 less over the oxide. In view of the value of ϵ_r for CF_3 on Si determined with VLPΦ[24a] and the comparable uptake of CF_2 and CF_3 suggested by Figure 2, it must be concluded that the principal loss mechanism in the LIF profiling experiments is polymerization of CF_2 on the surface. What is interesting about these results is that α_r for the vibrationally excited $v_2 = 1$ state of CF_2 is 50–70% larger than that for the vibrational ground state. Several authors[73,97] have suggested that vibrational excitation may contribute to surface reactivity, but little direct evidence for this has been available.

B. Nitrogen Fluorides on Silicon

Etching of silicon in NF_3 may be induced either by UV irradiation perpendicular to the surface[15,46] or infrared irradiation parallel to the surface.[47] The etching appears to be due primarily to the fluorine atom released in the NF_2 photolysis. While silicon is reported[44] not to be etched by NF_3, recent experiments in our laboratory[98] indicate that the NF_3–silicon surface reaction does occur. When a Si(100) surface is exposed to NF_3, the F(1s) XPS peak intensity shows an initial rapid increase; at higher NF_3 doses, the F(1s) intensity remains effectively constant. The F(1s) binding energy occurs at 687.2 eV, and shifts to slightly higher values at higher exposures to NF_3. This is indicative of dissociative chemisorption of NF_3 on Si(100) surfaces with buildup of a fluorinated silicon overlayer. The apparent saturation of coverage accounts for the lack of spontaneous etching[44] of silicon by NF_3, despite the facile surface reaction. The presence of an oxide layer on the surface, either thermally deposited or "native oxide", is sufficient to prevent the adsorption of NF_3. A small amount of nitrogen appears to be incorporated into the silicon following NF_3 exposure, but the extent of nitrogen incorporation varies with surface treatment. Nitrogen incorporation has been observed in silicon irradiated in the presence of NF_3–H_2 mixtures.[45] The reactions of silicon-containing surfaces with the NF_2 radical fragment have not yet been characterized.

C. Surface Reactions of Silicon Hydrides

Amorphous silicon thin films may be produced by photolysis of silane or organosilane,[53] mercury-photosensitized decomposition of silane,[61] plasma discharge CVD,[62] or thermally initiated CVD.[50] The SiH_2 radical is the principal silicon carrier to the surface in the photochemical processes[53] and in CVD processes initiated by homogeneous pyrolysis of silane,[50] viz.

$$SiH_4(g) \rightarrow SiH_2(g) + H_2(g) \qquad (4)$$

The reactive loss coefficient for SiH_2 on hydrogenated silicon–carbon surfaces has been measured as $\alpha_r = 0.1$ by the VLPΦ technique[99a] with IRMPD of *n*-butylsilane as the SiH_2 source. A value of $\alpha_r > 0.5$ is determined for vibrationally hot SiH_2, paralleling the higher reactivity found[81] for CF_2 in the $v_2 = 1$ state.

Even though the surface reactivity of SiH_2 has been reasonably well determined, there is some question as to whether this species plays a major role in the deposition kinetics. On the basis of modeling calculations, Gallagher[62] has concluded that 98% of neutral radical deposition in silane discharges results from SiH_3 radical deposition, although Perrin and Broekhuizen[61] find that ≥60% of adsorbed SiH_3 radicals recombine on the surface, rather than being incorporated into the film. In a recent publication,[99b] Scott et al. have questioned the radical mechanism and suggest that reaction of molecular SiH_4 and higher silanes at heated surfaces may account for much of the silicon deposition. There is an extensive literature on the deposition of amorphous silicon films, which has been the subject of previous reviews.[50]

D. Reactions of Atomic Free Radicals

Silicon and metallic surfaces are efficiently etched by halogen atoms generated by photolysis of suitable precursors. Systems that have been investigated include F/Si,[63,64] F/Mo,[63,64] F/Ti,[63] Cl/Si,[66,67,68a] Cl/Cr,[69b] Cl/Cu,[66,68b] Cl/Al, Cl/Ag, and Cl/Fe,[68a] Cl/Mo,[68a,69] Cl/W,[68a,69] and Br/GaAs.[65] Cl atoms are found not to etch gold films.[68a] When surface analysis is carried out,[68a] halogen incorporation is generally observed.

V. Discussion

A. A Bond Energy Model for Silicon Surface Reactions

A "zeroth-order" model based on the relative strengths of C–F, Si–F, Si–C, and Si–O bonds appears to be able to account for the observed behavior of CF_3 and CF_2 species on silicon and silicon oxide surfaces, as found in the experiments discussed in section IV.A. This model is based on a suggestion put forward by Joyce[4] and was used in a simple form by Oostra et al.[100] to explain their results on reactions of Ar^+-sputtered Si and SiO_2 in the presence of XeF_2 and Cl_2. The single-bond energies used in this model are given in Table II. While the bond energy values in the table are somewhat arbitrary, they are consistent with values in standard tables[101] and reference works.[102] In such a model, of course, neither lattice energies nor possible barriers to the surface reaction are considered. The likelihood of a specific surface reaction is determined from the same premise as that typically employed in gas-phase kinetics: an exothermic process *may* proceed, if the activation barrier is not too high, while an exothermic process is *not* likely to do so.

TABLE II. Single-Bond Energies (kJ mol^{-1}) Used in Surface Reaction Model

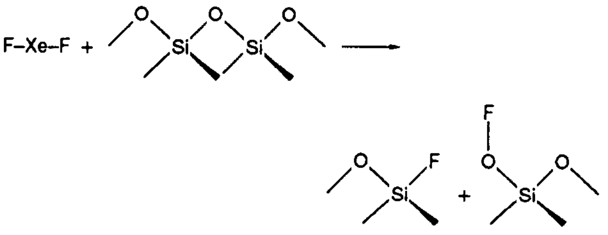
bond	energy	notes
Si–O	430	*a*
Si–F	550	*b–d*
Si–Si	180,[d,e] 330[c]	
C–F	460	*c, d*
Si–C	300	*f, d*
Xe–F	17	*c*
O–F	200	*g*
C–O	270	*c*
C=O	530	*c*
N–F	340,[c] 270[d]	
Si–N	439	*c*

[a] From value of 4.5 eV.[100] [b] From value of 5.6 eV.[100] [c] From ref 101. [d] From ref 102. [e] From value of 1.9 eV.[100] [f] Average of C–C and Si–Si single-bond energies; from ref 101. [g] Average of values from ref 101 and 102.

1. Xenon Difluoride on Silicon and Silicon Oxide

Xenon difluoride reacts spontaneously with silicon surfaces; at high exposures, an amorphous fluorosilyl overlayer is formed.[91a] The reaction is highly exothermic, and thus highly favored: for each fluorine atom (or silicon site), one Xe–F bond is broken (+17 kJ mol^{-1}) and one Si–F bond is formed (–550 kJ mol^{-1}), so the overall process is net 530 kJ mol^{-1} exothermic. Further reaction with bulk silicon is also favorable: whichever value for the bulk Si–Si bond energy one chooses from Table II, the formation of one Si–F bond at the expense of one Si–Si bond will be exothermic, and thus migration of fluorine into the silicon lattice proceeds spontaneously.

XeF_2 does *not* fluorinate a silicon oxide surface unless the surface has previously been damaged, e.g., by argon ion sputtering.[92] A possible reaction path is the following:

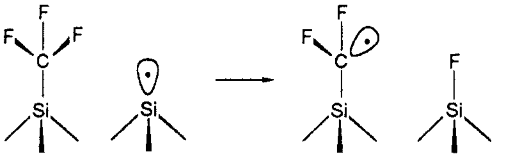


(5)

This process would require breaking two Xe–F bonds (at 17 kJ mol^{-1}) and one Si–O bond (430 kJ mol^{-1}), while forming one Si–F bond (550 kJ mol^{-1}) and one O–F bond (200 kJ mol^{-1}). The net enthalpy change is –286 kJ mol^{-1}, and so process (5) appears to be an exothermic reaction that should proceed spontaneously. The observation[92] that it does not do so implies that there must be a substantial barrier to the reaction; the corresponding lack of reactivity of other valence-saturated species, such as CF_4 on Si, suggests that a barrier is present in these systems as well. The effect of surface damage (e.g., ion bombardment) in promoting the reaction would then be to reduce the barrier to chemisorption by creating new binding sites; in this case, silicon suboxides are likely to be the predominant active sites.

2. *Trifluoromethyl on Silicon*

CF_3 radicals bind readily to the "dangling bonds" at the silicon surface,[29] with an exothermicity of ~300 kJ mol^{-1} arising from formation of a new C–Si bond. Subsequent transfer of fluorine atoms from the CF_3 group to neighboring Si surface sites is also favored



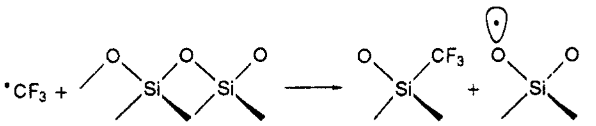
(6)

since the formation of a Si–F bond (550 kJ mol^{-1}) at the expense of a C–F bond (460 kJ mol^{-1}) is −90 kJ mol^{-1} exothermic. As electronegative fluorine atoms are removed from the carbon adatom, the C–F bond strength may increase,[103] so that removal of the last fluorine atom becomes less favorable; XPS analyses of CF_3-dosed silicon surfaces indicated[29] that some of the chemisorbed fluorocarbon was present in the form of CF.

It was also found[29] that adventitious carbon, while not inhibiting the adsorption of CF_3, did block the fluorine atom transfer reaction (6). This can be understood by noting that rupturing a preexisting Si–C bond requires an additional 300 kJ mol^{-1}, which converts the process from −90 kJ mol^{-1} exothermic to +210 kJ mol^{-1} endothermic.

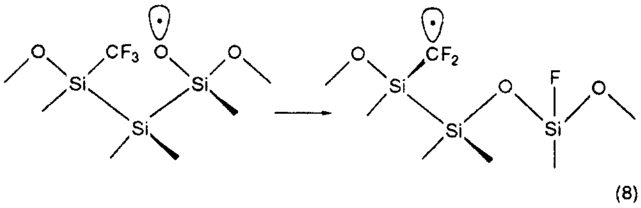
3. *Trifluoromethyl on Silicon Oxide*

The sticking probability of CF_3 on an annealed oxide surface is considerably less than on a silicon surface,[30] since adsorption of CF_3 would require breaking a Si–O bond (+430 kJ mol^{-1}) while gaining only −300 kJ mol^{-1} from the newly formed Si–C bond:



(7)

As is the case with XeF_2 chemisorption, weakening or breaking one of the Si–O bonds by ion bombardment can convert this net endothermic process to a net exothermic one. Even if the CF_3 is chemisorbed, little or no carbon-to-silicon transfer of fluorine atoms takes place on oxide surfaces.[30] A process such as

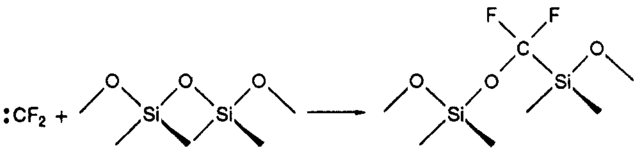


(8)

would be net exothermic (a Si–F bond and a Si–O bond are made at the expense of a Si–Si bond and a C–F bond), but evidently the lattice rearrangement that would be required to accommodate reaction 8 is sufficiently great to prevent its occurrence. No simple exothermic F-transfer processes are apparent in which the silicon lattice is undisturbed.

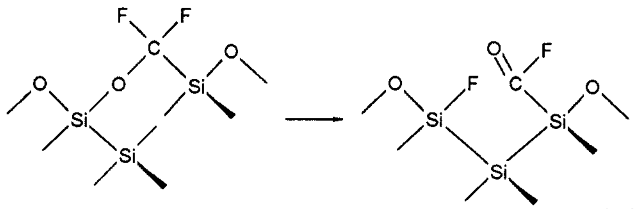
4. *Difluorocarbene on Silicon and Silicon Oxide*

As with CF_3, the difluorocarbene radical binds readily to dangling bonds on a silicon surface (−300 kJ mol^{-1} exothermic) and transfers fluorine to neighboring silicon sites (−90 kJ mol^{-1} exothermic). It was found[42] that CF_2 binds much more readily to an annealed oxide surface than does CF_3. This can result from an insertion reaction



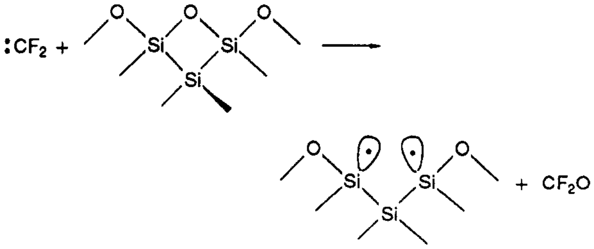
(9)

in which a new Si–C bond (−300 kJ mol^{-1}) and a new C–O bond (−270 kJ mol^{-1}) are produced, compensating for the energy required (+430 kJ mol^{-1}) in the Si–O bond-breaking step. Fluorine atom transfer to silicon sites still does not occur on an oxide surface; the least unfavorable path, in which C–F and Si–O bonds are broken, an Si–F bond is made, and a C–O bond acquires some double-bond character



(10)

would still be approximately +80 kJ mol^{-1} endothermic. Suggestions that silicon oxide may be directly etched by CF_2 by removing oxygen and leaving Si "dangling bonds" on the surface, i.e.



(11)

are also incompatible with this model: reaction 11 would be endothermic by more than 300 kJ mol^{-1}.

5. *Discussion of Bond Energy Model*

Our preliminary results[98] for NF_3 on silicon and silicon oxide surfaces are consistent with this proposed model. For chemisorption on the silicon surface, bonds would have to be broken, and Si–N bond formation is exothermic; the nitrogen in this case would possess more than the typical octet of valence electrons, but due to its electronegativity and that of fluorine, this may not be unlikely. After chemisorption, the process of fluorine transfer is exothermic (–480 to –650 kJ mol^{-1}) and seems to go to completion, simultaneously fluorinating and partially nitriding the surface. Even a few monolayers of oxide are sufficient to block the adsorption of NF_3, since the corresponding process becomes significantly endothermic if Si–O bonds have to be broken.

While such bond energy considerations are successful in explaining a number of results, including the relative reactivity of silicon surfaces to XeF_2 and to Cl_2,[100] this model clearly does not account for all the observed phenomena. The thermochemical model does not take account of energy changes associated with lattice rearrangement or surface reconstruction[124] nor of possible barriers to chemisorption.[125] The importance of barriers is clearly demonstrated by the lack of reactivity of valence-saturated molecular species on surfaces at which the net reaction would appear to be exothermic: F_2 on Si,[126] XeF_2 on SiO_2,[92] and undissociated fluorocarbons such as CF_4 on Si are examples. An activation energy of approximately 80 kJ mol^{-1} was inferred from Suzuki's measurements of Si etch rate with a hot SF_6 beam,[105] again suggesting a barrier to dissociative chemisorption in this system. In the case of NF_3, the initial chemisorption step is so exothermic (–650 kJ mol^{-1}) that the barrier, if present, can be overcome at room temperature; reaction on the oxide, however, would be endothermic and is predicted not to occur. Further development of this model will need to consider both lattice rearrangement and surface reconstruction energies as well as energy barriers along the reaction path. At the current level of ab initio theory, such calculations for realistic surface models are now becoming possible.

B. Comparison with Plasma-Etching Models

One of the objectives of the investigations reviewed in this article has been to clarify the role of neutral free radicals in plasma reactive etching. The results that have been obtained validate many of the conclusions reached by Coburn et al.[106] in their important early work on etching in fluorocarbon plasmas. They found that at low coverage, all the surface fluorine is bonded to silicon, and at higher coverage C–F bonds are observed on the surface. These results suggest that initially, CF_3 dissociatively chemisorbs on Si but dissociation is inhibited when surface binding sites are occupied. This is seen to be a reaction characteristic of the neutral CF_3 radical itself. They found that carbon accumulates on a silicon but not a silicon oxide surface, showing that CF_3 does not readily chemisorb on the oxide. Their suggestion that production of surface damage by ion bombardment facilitates reaction of neutral free radicals on the surface is certainly true for the oxide. However, the photochemical studies show that the selectivity for etching oxide vs silicon in "CF_2-rich" plasmas cannot be attributed simply to higher reactivity of silicon oxide with CF_2. The suggestions that CF_2 may participate in the etching of silicon oxide by removing oxygen and leaving Si "dangling bonds" on the surface are not borne out by either the experimental results of ref 42 or the analysis presented in the preceding section. The identity of the species responsible for etching silicon oxide remains an open question.

C. Potential Applications for Laser-Initiated Free-Radical Chemistry at Surfaces

While the principal thrust of the work described in this review has been to achieve a better understanding of the surface chemistry occurring between free radicals and electronic materials, such as silicon, there are also a number of potential applications based on laser-initiation techniques that can be envisioned. A number of these, such as direct writing of conducting and insulating components in electronic microcircuits, have been covered in reviews by Baüerle[5] and Houle.[6] Here, we mention some recent additional developments. These include epitaxial growth of Ge films on GaAs by LCVD from germane vapor photolyzed by an ArF laser[107] and fabrication of superlattice structures containing silicon, germanium, and silicon nitride by 193-nm photolysis of disilane–germane–ammonia mixtures.[108] Recent surveys[109a,b] have concluded that beam-controlled processing techniques, including photon-driven methods, have been the key to current achievements in microcircuit integration and density and are likely to lead to new fabrication advances in the future.

In addition to electronic devices, laser microfabrication of optical elements, such as silicon nitride and silicon oxide "microlenses", have been reported.[110] "Diamond-like" carbon films have eventual applications in a number of technologies, including electronics and optics.[111] Formation of such films by excimer laser photolysis of C_2H_2–H_2 mixtures has been reported,[112] and it has been shown[113,114] that ArF excimer laser photolysis of acetylene involves free radicals such as $C_2(^3\Pi)$, CH, and C_2H. Laser-initiated processes also can be useful as diagnostics for surface processes, such as measurement of surface diffusion by localized surface photochemistry.[115]

Finally, we should mention the possibility of laser-processing techniques for fabrication of high-T_c superconducting materials.[116] While production of copper oxide superconductors by CVD from the β-diketonates has only recently been reported,[117] the use of lasers for this process has thus far been limited to ablative transfer of the material from a prepared solid substrate to a thin film, using either excimer[118–121] or CO_2[122] lasers, or to laser patterning of metal neodecanoates layered on $SrTiO_3$ substrate.[123] Direct LCVD production of superconducting thin films, in which free-radical reactions may play a role, is a clear possibility.

D. Conclusions

The use of laser-initiation methods has enabled us to obtain detailed information on free-radical reactions at surfaces, particularly those of semiconductors and other electronic materials. In addition to providing a better understanding of the chemical reactions involved in processes such as reactive etching and vapor deposition, the laser techniques may be directly applicable to advanced fabrication methods. As more complex processing methods are developed, particularly involving mixtures of reactive gas-phase species, a full understanding of the free-radical reactions and surface chemistry will be required in order to optimize such processes and develop new ones.

Acknowledgments. While it is a pleasure to be able to acknowledge the contributions of numerous collab-

orators, I wish to note in particular the late Dr. John R. Hollahan, who first turned my attention to the intriguing subject of laser effects on silicon surface chemistry. The work described in this review was carried out by a series of dedicated graduate students and postdoctoral associates, including Bobbi Roop, Steve Joyce, Jay Thoman, Keizo Suzuki, Jocelyn Schultz, John Langan, Xu Xin, and Jeff Shorter. I also wish to thank the many colleagues who assisted us in our forays into surface chemistry, including Dr. F. R. McFeely (now at I.B.M.), Professor Sylvia Ceyer, Dr. F. Walsh (Tracer Technologies), Dr. C. B. Zarowin (Perkin-Elmer), and Dr. M. Kanal (Digital Equipment Corp.). Financial support was provided by the Air Force Office of Scientific Research (Contract F49620-86-C-0003), the National Science Foundation (Industry–University Cooperative Grant CHE81-21472 and Chemistry Division Grant CHE86-02986), Digital Equipment Corp., and graduate fellowships from the Lyons Foundation and Perkin-Elmer Corp.

VI. References and Notes

(1) Paneth, F.; Hofeditz, W. *Ber. Chem. Ges.* **1929**, *62*, 1335.

(2) (a) Rice, F. O. *J. Am. Chem. Soc.* **1931**, *53*, 1959. (b) Rice, F. O.; Johnston, W. R.; Evering, B. L. *J. Am. Chem. Soc.* **1932**, *54*, 3529. (c) Rice, F. O.; Glasebrook, A. L. *J. Am. Chem. Soc.* **1934**, *56*, 2381.

(3) Herzberg, G. *The Spectra and Structures of Simple Free Radicals*; Cornell University Press: Ithaca, NY, 1971; p 2.

(4) Joyce, S. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1987.

(5) Baüerle, D. *Chemical Processing with Lasers*; Springer-Verlag: Berlin, 1986.

(6) Houle, F. A. *Appl. Phys.* **1986**, *A41*, 315.

(7) Steinfeld, J. I. *Laser-Induced Chemical Processes*; Plenum Press: New York, 1981.

(8) Francisco, J. S.; Steinfeld, J. I. In *Advances in Multiphoton Processes and Spectroscopy*; Lin, S. H., Ed.; World Scientific Publishing Pte Ltd.: Singapore, 1986; Vol. 2, pp 79–173.

(9) Lupo, D.; Quack, M. *Chem. Rev.* **1987**, *87*, 181.

(10) Flamm, D. L.; Donnelly, V. M.; Ibbotson, D. E. *J. Vac. Sci. Technol.* **1983**, *B1*, 23.

(11) (a) Suto, M.; Washida, N. *J. Chem. Phys.* **1983**, *78*, 1007, 1012. (b) Suto, M.; Washida, N.; Akimoto, H.; Nakamura, M. *J. Chem. Phys.* **1983**, *78*, 1019. (c) Washida, N.; Suto, M.; Nagase, S.; Nagashima, U.; Morokuma, K. *J. Chem. Phys.* **1983**, *78*, 1025.

(12) Quick, C. R., Jr.; Tiee, J. J.; Preses, J.; Weston, R. E., Jr. *Chem. Phys. Lett.* **1985**, *114*, 371.

(13) Dreyfus, R. W.; Urbach, L. *Chem. Phys. Lett.* **1985**, *114*, 376.

(14) (a) Brewer, P.; Halle, S.; Osgood, R. M. *Mater. Res. Soc. Symp. Proc.* **1984**, *29*, 179. (b) Brewer, P.; Halle, S.; Osgood, R. M., Jr. *Appl. Phys. Lett.* **1984**, *45*, 475.

(15) Armacost, M. D.; Babu, S. V.; Nguyen, S. N.; Rembetski, J. F. *J. Mater. Res.* **1987**, *2*, 895.

(16) Rossi, M. J.; Barker, J. R.; Golden, D. M. *J. Chem. Phys.* **1979**, *71*, 3722.

(17) Quack, M.; Seyfang, G. *J. Chem. Phys.* **1982**, *76*, 955.

(18) Gauthier, M.; Nip, W. S.; Hackett, P. A.; Willis, C. *Chem. Phys. Lett.* **1980**, *69*, 372.

(19) Sarkar, S. K.; Parthasarathy, V.; Pandey, A.; Rama Rao, K. V. S.; Mittal, J. P. *Chem. Phys. Lett.* **1981**, *78*, 479.

(20) Hackett, P.; Gauthier, M.; Willis, C. *J. Chem. Phys.* **1978**, *69*, 2924.

(21) Fuss, W.; Kompa, K. L.; Tablas, F. M. G. *Faraday Discuss. Chem. Soc.* **1979**, *67*, 180.

(22) Selamoglu, N.; Rossi, M. J.; Golden, D. M. *J. Chem. Phys.* **1986**, *84*, 2400.

(23) Robertson, R. M.; Rossi, M. J.; Golden, D. M. *J. Vac. Sci. Technol.* **1987**, *A5*, 3351.

(24) (a) Robertson, R. M.; Golden, D. M.; Rossi, M. J. *J. Vac. Sci. Technol.* **1988**, *A6*, 1407. (b) Robertson, R. M.; Golden, D. M.; Rossi, M. J. *J. Chem. Phys.* **1988**, *89*, 2925.

(25) Steinfeld, J. I.; Anderson, T. G.; Reiser, C.; Denison, D. R.; Hartsough, L. D.; Hollahan, J. R. *J. Electrochem. Soc.* **1980**, *127*, 514.

(26) Fisk, G. A. *Chem. Phys. Lett.* **1978**, *60*, 11.

(27) Horwitz, A. B.; Preses, J. M.; Weston, R. E., Jr.; Glynn, G. *J. Chem. Phys.* **1981**, *74*, 5008.

(28) Arai, S.; Watanabe, T.; Ishikawa, Y.; Oyama, T. *Chem. Phys. Lett.* **1984**, *112*, 224.

(29) Roop, B.; Joyce, S.; Schultz, J. C.; Steinfeld, J. I. *J. Chem. Phys.* **1985**, *83*, 6012.

(30) Joyce, S.; Langan, J. G.; Steinfeld, J. I. *J. Chem. Phys.* **1988**, *88*, 2027.

(31) Würzberg, E.; Kovalenko, L. J.; Houston, P. L. *Chem. Phys.* **1978**, *35*, 317.

(32) Sudbo, Aa. S.; Schulz, P. A.; Grant, E. R.; Shen, Y. R.; Lee, Y. T. *J. Chem. Phys.* **1979**, *70*, 912.

(33) Thoman, J. W., Jr. Ph.D. Thesis, Massachusetts Institute of Technology, 1987, pp 83–85.

(34) (a) King, D. S.; Stephenson, J. C. *Chem. Phys. Lett.* **1979**, *66*, 33. (b) Stephenson, J. C.; King, D. S.; Goodman, M. F.; Stone, J. *J. Chem. Phys.* **1979**, *70*, 4496.

(35) (a) Herman, I. P.; Marling, J. *J. Chem. Phys.* **1979**, *71*, 643. (b) Herman, I. P.; Marling, J. *J. Chem. Phys.* **1980**, *72*, 516.

(36) Tuccio, S. A.; Hartford, A., Jr. *Chem. Phys. Lett.* **1979**, *65*, 235.

(37) Krajnovich, D.; Zhang, Z.; Butler, L.; Lee, Y. T. *J. Phys. Chem.* **1984**, *88*, 4561.

(38) At 193 nm, single-photon production of $CF_2 + Br_2$ may be a possibility.

(39) Brannon, J. H. *J. Phys. Chem.* **1986**, *90*, 1784.

(40) (a) Loper, G. L.; Tabat, M. D. *Proc. 17th Int. Symp. Free Radicals*, Granby, CO, 1985; *NBS Spec. Publ. No. 716*, **1986**, pp 468–481. (b) Loper, G. L.; Tabat, M. D. *Proc. SPIE* **1984**, *459*, 121.

(41) Sharpe, S.; Hartnett, B.; Sethi, H. S.; Sethi, D. S. *J. Photochem.* **1987**, *38*, 1.

(42) Langan, J. G.; Shorter, J. A.; Xu Xin; Joyce, S. A.; Steinfeld, J. I. *J. Surf. Sci.* **1989**, *207*, 344.

(43) (a) Chow, T. P.; Steckl, A. J. *J. Appl. Phys.* **1982**, *53*, 5531. (b) Donnelly, V. M.; Flamm, D. L.; Dautremont-Smith, W. C.; Werder, D. J. *J. Appl. Phys.* **1984**, *55*, 242. (c) Barkanic, J.; Hoff, A.; Stach, J.; Golja, B. In *Semiconductor Processing ASTM STP 850*; Gupta, D. C., Ed.; American Society for Testing Materials: Philadelphia, 1984.

(44) Ibbotson, D. E.; Mucha, J. A.; Flamm, D. L.; Cook, J. M. *J. Appl. Phys.* **1984**, *56*, 2939.

(45) Yokoyama, S.; Yamakage, Y.; Hirose, M. *Appl. Phys. Lett.* **1985**, *47*, 389.

(46) Loper, G. L.; Suck Salk, S. H.; Tabat, M. D. *Symp. Laser Proc. Microelectronics Appl.*, Honolulu, 1987; Paper No. 438.

(47) Brannon, J. H. *Appl. Phys.* **1988**, *A46*, 39.

(48) Heidner, R. F., III; Helvajian, H.; Koffend, J. B. *J. Chem. Phys.* **1987**, *87*, 1521.

(49) O'Hanlon, J. F.; Fraser, D. E. "Recommended Practices for Pumping Hazardous Gases". *J. Vac. Sci. Technol. A* **1988**, *A6*, 1226.

(50) Jasinski, J. M.; Meyerson, B. S.; Scott, B. A. *Annu. Rev. Phys. Chem.* **1987**, *38*, 109.

(51) Deutsch, T. F. *J. Chem. Phys.* **1979**, *70*, 1187.

(52) Millot, G.; Hetzler, J.; Foy, B.; Steinfeld, J. I. *J. Chem. Phys.* **1988**, *88*, 6742.

(53) Francisco, J. S.; Joyce, S. A.; Steinfeld, J. I.; Walsh, F. *J. Phys. Chem.* **1984**, *88*, 3098.

(54) Inoue, G.; Suzuki, M. *Chem. Phys. Lett.* **1984**, *105*, 641.

(55) Rayner, D. M.; Steer, R. P.; Hackett, P. A.; Wilson, C.; John, P. *Chem. Phys. Lett.* **1986**, *123*, 449.

(56) Thoman, J. W., Jr.; Steinfeld, J. I. *Chem. Phys. Lett.* **1986**, *124*, 35.

(57) Thoman, J. W., Jr.; Steinfeld, J. I.; McKay, R. I.; Knight, A. E. W. *J. Chem. Phys.* **1987**, *86*, 5909.

(58) Francisco, J. S.; Schlegel, H. B. *J. Chem. Phys.* **1988**, *88*, 3736.

(59) Van Zoeren, C. M.; Thoman, J. W., Jr.; Steinfeld, J. I.; Rainbird, M. W. *J. Phys. Chem.* **1988**, *92*, 9.

(60) Uichanco, A. S.; Knight, A. E. W., to be published.

(61) Perrin, J.; Broekhuizen, T. *Appl. Phys. Lett.* **1987**, *50*, 433.

(62) Gallagher, A. *J. Appl. Phys.* **1988**, *63*, 2406.

(63) Loper, G. L.; Tabat, M. D. *Appl. Phys. Lett.* **1985**, *46*, 654.

(64) Loper, G. L.; Tabat, M. D. *J. Appl. Phys.* **1985**, *58*, 3649.

(65) Brewer, P. D.; McClure, D.; Osgood, R. M., Jr. *Appl. Phys. Lett.* **1985**, *47*, 310.

(66) van Veen, G. N. A.; Baller, T.; Dieleman, J.; de Vries, A. E. *J. Vac. Sci. Technol.* **1987**, *A5*, 1606.

(67) Kullmer, R.; Baüerle, D. *Appl. Phys.* **1987**, *A43*, 227.

(68) (a) Sesselman, W.; Chuang, T. J. *J. Vac. Sci. Technol.* **1985**, *B3*, 1507. (b) Sesselman, W.; Marinero, E. E.; Chuang, T. J. *Appl. Phys.* **1986**, *A41*, 209.

(69) (a) Rothschild, M.; Sedlacek, J. H. C.; Ehrlich, D. J. *Appl. Phys. Lett.* **1986**, *49*, 1554. (b) Rothschild, M.; Sedlacek, J. H. C.; Black, J. G.; Ehrlich, D. J. *J. Vac. Sci. Technol.* **1987**, *B5*, 414. (c) Rothschild, M.; Sedlacek, J. N. C.; Ehrlich, D. J. *J. Vac. Sci. Technol.* **1987**, *B5*, 1400.

(70) (a) Irvine, S. J. C. *CRC Crit. Rev. Solid State Mater. Sci.* **1987**, *13*, 279. (b) Ray, U.; Brandow, S. L.; Bardukwalla, G.; Venkataraman, B. K.; Zhang, Z.; Vernon, M. *J. Chem. Phys.* **1988**, *89*, 4092. (c) Waller, I. M.; Davis, H. F.; Hepburn, J. W. *J. Phys. Chem.* **1987**, *91*, 506. (d) Gluck, N. S.; Wolga, G. J.; Bartosch, C. E.; Ho, W.; Ying, Z. *J. Appl. Phys.* **1987**, *61*, 998. (e) Xu Xin; Bellon, S.; Steinfeld, J. I. *Proc. Mater. Res. Soc. Symp.*, Boston, MA, Dec 1988. (f) Baüerle, D. *Laser Processing and Diagnostics*; Springer-Verlag: Berlin, 1984.

(71) Ehrlich, D. J.; Osgood, R. M., Jr.; Deutsch, T. F. *J. Electrochem. Soc.* **1981**, *128*, 2039.

(72) Krchavnek, R. R.; Gilgen, H. H.; Chen, J. C.; Shaw, P. S.; Licata, T. J.; Osgood, R. M., Jr. *J. Vac. Sci. Technol.* **1987**, *B5*, 20.

(73) (a) Chuang, T. J. *J. Chem. Phys.* **1980**, *72*, 6303. (b) Chuang, T. J. *J. Chem. Phys.* **1981**, *74*, 1453.

(74) Chang, R. K.; Furtak, T. E., Eds. *Surface Enhanced Raman Scattering*; Plenum Press: New York, 1982.

(75) Moskovits, M. *Rev. Mod. Phys.* **1985**, *57*, 783.

(76) Köser, M. J. K. *Spectrochim. Acta* **1984**, *40A*, 117, 547.

(77) Rosencwaig, A. *Photoacoustics and Photoacoustic Spectroscopy*; Wiley: New York, 1980.

(78) (a) Patel, C. K. N.; Tam, A. C. *Rev. Mod. Phys.* **1981**, *53*, 517. (b) Tam, A. C. *Rev. Mod. Phys.* **1986**, *58*, 381.

(79) (a) Higashi, G. S.; Rothberg, L. J.; Fleming, C. G. *Chem. Phys. Lett.* **1985**, *115*, 167. (b) Brueck, S. R. J.; Deutsch, T. F.; Oates, D. E. *Appl. Phys. Lett.* **1983**, *43*, 157. (c) Coufal, H.; Chang, T. J.; Träger, F. *J. Phys.* **1983**, 44–66, 297.

(80) Tanaka, K.; Ichimura, Y.; Sindoh, K. *J. Appl. Phys.* **1988**, *63*, 1815.

(81) Thoman, J. W., Jr.; Suzuki, K.; Kable, S. H.; Steinfeld, J. I. *J. Appl. Phys.* **1986**, *60*, 2775.

(82) (a) Hata, N.; Matsuda, A.; Tanaka, K. *Jpn. J. Appl. Phys.* **1986**, *25*, 108. (b) Hata, N.; Matsuda, A.; Tanaka, K. *J. Appl. Phys.* **1986**, *59*, 1872. (c) Hata, N.; Matsuda, A.; Tanaka, K. *J. Appl. Phys.* **1987**, *61*, 3055. (d) Robertson, R. M.; Golden, D. M.; Rossi, M. J. *J. Phys. Chem.* **1988**, *92*, 5338.

(83) Auerbach, D. J.; Becker, C. A.; Cowing, J. P.; Wharton, L. *Rev. Sci. Instrum.* **1973**, *49*, 1518.

(84) Roop, B. Ph.D. Thesis, Massachusetts Institute of Technology, 1985.

(85) Helms, A. L., Jr.; Schiedt, W. A.; Bernasek, S. L.; Biwer, B. M. *Rev. Sci. Instrum.*, in press.

(86) Ninomiya, K.; Suzuki, K.; Nishimatsu, S.; Gotoh, Y.; Okada, O. *J. Vac. Sci. Technol.* **1984**, *B2*, 645.

(87) Chen, C. J. *J. Vac. Sci.* **1987**, *A5*, 3386.

(88) (a) Skouby, D. C.; Jensen, K. F. *J. Appl. Phys.* **1988**, *63*, 198. (b) Copley, S. M. *J. Appl. Phys.* **1988**, *64*, 2064. (c) Kodas, T. T.; Comita, P. B. *J. Appl. Phys.*, in press.

(89) (a) Dixon-Warren, St. J.; Harrison, I.; Leggett, K.; Matyjaszczyk, M. S.; Polanyi, J. C.; Young, P. A. *J. Chem. Phys.* **1988**, *88*, 4052. (b) For a general discussion of laser damage to surfaces, see: Ready, J. F. *Effects of High-Power Laser Radiation*; Academic Press: New York, 1971.

(90) Suzuki, K., unpublished results.

(91) (a) Roop, B.; Joyce, S.; Schultz, J. C.; Steinfeld, J. I. *Surf. Sci.* **1986**, *173*, 455. (b) Winters, H. F.; Houle, F. A. *J. Appl. Phys.* **1983**, *54*, 1218. (c) McFeely, F. R.; Morar, J. F.; Shinn, N. D.; Landgren, G.; Himpsel, F. J. *Phys. Rev.* **1984**, *B30*, 764.

(92) Joyce, S.; Langan, J. G.; Steinfeld, J. I. *Surf. Sci.* **1988**, *195*, 270.

(93) Joyce, S.; Langan, J., unpublished results.

(94) Vasile, M. J.; Stevie, F. A. *J. Appl. Phys.* **1982**, *53*, 3799.

(95) (a) McFeely, F. R.; Yarmoff, J. A.; Beach, D. B. *J. Chem. Phys.* **1988**, *89*, 7609. (b) McFeely, F. R.; Yarmoff, J. A.; Taleb-Ibrahimi, A.; Beach, D. B., to be published.

(96) Larsen, P. K.; Feiner, L. F.; Friedel, P. *Phys. Rev.* **1987**, *B35*, 757.

(97) Gerlach-Meyer, U. *Surf. Sci.* **1981**, *103*, 524.

(98) Steinfeld, J. I.; Shorter, J. A.; Langan, J.; Xu Xin, *SPIE Proc.* *1056* (O/E-LASE Symposium, Los Angeles, CA, Jan 1989).

(99) (a) Robertson, R. M.; Rossi, M. J., to be published. (b) Scott, B. A.; Estes, R. D.; Jasinski, J. M. *J. Chem. Phys.* **1988**, *89*, 2544.

(100) Oostra, J. D.; Haring, A.; de Vries, A. E. *J. Vac. Sci. Technol.* **1986**, *B4*, 1278.

(101) Weast, R. C., Ed. *CRC Handbook of Chemistry and Physics*, 67th ed.; CRC Press: Boca Raton, FL, 1986; pp F-167 to F-184.

(102) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960; p 85.

(103) The C–F bond dissociation energy in the diatomic radical is 5.67 eV or 550 kJ/mol,[101,104] approximately equal to the Si–F bond energy.

(104) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure IV, Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979; p 138.

(105) (a) Suzuki, K.; Ninomiya, K.; Nishimatsu, S.; Okada, O. *Jpn. J. Appl. Phys.* **1986**, *25*, L373. (b) Suzuki, K.; Ninomiya, K.; Nishimatsu, S.; Okada, O. *Jpn. J. Appl. Phys.* **1987**, *26*, 166. (c) Suzuki, K.; Ninomiya, K.; Nishimatsu, S.; Okada, O. *J. Vac. Sci. Technol.* **1987**, *A5*, 1605.

(106) Coburn, J. W.; Winters, H. F.; Chuang, T. J. *J. Appl. Phys.* **1977**, *77*, 3532.

(107) Tavitian, V.; Kiely, C. J.; Geohegan, D. B.; Eden, J. G. *Appl. Phys. Lett.* **1988**, *52*, 1710.

(108) Lowndes, D. H.; Geohegan, D. B.; Eres, D.; Pennycook, S. J.; Mashburn, D. N.; Jellison, G. E., Jr. *Appl. Phys. Lett.* **1988**, *52*, 1868.

(109) (a) Kern, D. P.; Kuech, T. F.; Oprysko, M. M.; Wagner, A.; Eastman, D. E. *Science* **1988**, *241*, 936. (b) Kompa, K. L. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1389.

(110) Sugimura, A.; Fukada, Y.; Hanabusa, M. *J. Appl. Phys.* **1988**, *62*, 3222.

(111) Angus, J. C.; Hayman, C. C. *Science* **1988**, *241*, 913.

(112) Kitahama, K.; Hirata, K.; Nakamatsu, H.; Kawai, S.; Fujimori, N.; Imai, T.; Yoshino, H.; Doi, A. *Appl. Phys. Lett.* **1986**, *49*, 634.

(113) Okabe, H.; Cody, R. J.; Allen, J. E., Jr. *Chem. Phys.* **1985**, *92*, 67.

(114) Irion, M. P.; Kompa, K. L. *Appl. Phys.* **1982**, *B27*, 183.

(115) Tsao, J. Y.; Zeiger, H. J.; Ehrlich, D. J. *Surf. Sci.* **1985**, *160*, 419.

(116) Murphy, D. W.; Johnson, D. W., Jr.; Jin, S.; Howard, R. E. *Science* **1988**, *241*, 922.

(117) Berry, A. D.; Gaskill, D. K.; Holm, R. T.; Cukauskas, E. J.; Kaplan, R.; Henry, R. L. *Appl. Phys. Lett.* **1988**, *52*, 1743.

(118) Dijkkamp, D.; Venkatesan, T.; Wu, X. D.; Shaheen, S. A.; Jisrawi, N.; Min-Lee, Y. H.; McLean, W. L.; Croft, M. *Appl. Phys. Lett.* **1978**, *51*, 619.

(119) Wu, X. D.; Dijkkamp, D.; Ogale, S. B.; Inam, A.; Chase, E. W.; Miceli, P. F.; Chang, C. C.; Tarascon, J. M.; Venkatesan, T. *Appl. Phys. Lett.* **1987**, *51*, 861.

(120) Inam, A.; Wu, X. D.; Venkatesan, T.; Ogale, S. B.; Chang, C. C.; Dijkkamp, D. *Appl. Phys. Lett.* **1987**, *51*, 1112.

(121) Venkatesan, T.; Chang, C. C.; Dijkkamp, D.; Ogale, S. B.; Chase, E. W.; Farrow, L. A.; Hwang, D. M.; Micelli, P. F.; Schwarz, S. A.; Tarascon, J. M.; Wu, X. D.; Inam, A. *J. Appl. Phys.*, in press.

(122) Miura, S.; Toshitake, T.; Satoh, T.; Miyasaka, Y.; Shohata, N. *Appl. Phys. Lett.* **1988**, *52*, 1008.

(123) Mantese, J. V.; Catalan, A. B.; Mance, A. M.; Hamdi, A. H.; Micheli, A. L.; Sell, J. A.; Meyer, M. S. *Appl. Phys. Lett.* **1988**, *53*, 1335.

(124) Oppenheim, I.; Levine, R. D., to be published.

(125) Ceyer, S. T. *Annu. Rev. Phys. Chem.* **1988**, *39*, 479.

(126) Mucha, J. A.; Donnelly, V. M.; Flamm, D. L.; Webb, L. M. *J. Phys. Chem.* **1981**, *85*, 3529.