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# Invited

## Laser Induced Gas-Surface Chemistry and Photoetching of Solids

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Recent studies have shown the potential of laser-assisted surface photochemistry to become powerful means for processing electronic materials. Here a brief summary of these investigations is given. The basic photochemical processes at the gas-solid interfaces including the photon-enhanced chemisorption, adsorbate-adsorbate and molecule-solid reactions, product formation and desorption of surface species are outlined. Some model reaction systems related in particular to photoetching of solid surfaces are discussed.

#### 1. Introduction

Lasers have been extensively used in recent years to induce or enhance chemcal interactions at gassolid interfaces. The rapid expansion of the field which can be generally referred as laser-induced gas-surface chemistry is driven by both the basic scientific interest and the potential technological applications in material processing and fabrication of new materials. In the basic area, there are fundamental questions concerning energy transformation from photons into chemical energies, the kinetics and dynamic processes involving energy acquisition, storage and decay that need to be understood. In the applied area, related in particular to material processing, the laser photochemical techniques have shown great promises in producing well-defined microstructures for electronic devices. Other potential applications such as photocatalytic reactions and energy conversions will undoubtedly be further developed in the future. These basic and applied aspects of the laser surface chemistry have been a subject of a few reviews appeared recently /1-3/. Here, a brief review is presented on the important surface processes stimulated by laser radiation, with particular emphases on recent mechanistic studies related to photochemical etching and deposition of solid materials. For more general considerations and thorough discussions, one should refer to prior reviews /1-3/.

## 2. Basic Laser Stimulated Surface Processes

A molecule-surface reaction usually involves adsorption, dissociative chemisorption, adsorbateadsorbate and adsorbate-solid reaction, product formation and desorption of surface species. Photon beams can influence and in many cases enhance these processes via photoexcitation of gaseous species, the adsorbates and/or solid atoms. The modes of excitation include the vibrational and electronic states of the gaseous species and the adsorbate-surface complexes, and the electronic as well as the thermal activation of the substrate. Both the single and the multiple photon absorption may be involved in the excitation process. A noted example to demonstrate the photoenhanced chemisorption and reaction due to vibrational excitation is the interaction of SF<sub>6</sub> with silicon /4/. It was shown that although the molecules were inert to Si at 25°C, they could be chemically activated by multiple photon absorption of CO<sub>2</sub> laser photons either in the gas phase or in the adsorbed state. A systematic study was performed including the determination of reaction yields as a function of the laser wavelength, the laser intensity and the gas pressure as well as the reaction products. Reactive radicals generated by multiple infrared photon dissociation to react with surfaces resulted in chemical etching of solids were also observed on Si /4/ and SiO<sub>2</sub> /5/. IR multiple photon excitation was also used

to decompose  $\text{SiH}_4$  molecules for deposition of Si on quartz and glass substrates /6/.

Likewise, photodissociation to produce radicals can be accomplished by single photon absorption in the ultraviolet (UV) and visible spectral regions. The radicals can often react with surfaces which are inert to the parent molecules. Many surface etching and vapor deposition reactions are activated by such a photochemical process. The prominent examples are Si/Cl<sub>2</sub> /7/ and SiO<sub>2</sub>/Cl<sub>2</sub> /8/ surface etching reactions enhanced by an Ar<sup>+</sup> laser, and metal deposition on quartz substrates by UV photolysis of Al(CH3)3 and Cd(CH3)2 /9/. Electronic excitation of solid substrates can also effectively enhance the surface reaction, most notably the band gap excitation of oxide and semiconductor surfaces. Photoenhanced oxidation of Si /10/ and GaAs /11/, and etching of Si by XeF<sub>2</sub> /12/ are noted examples. Electronic excitation effects other than the thermal effects on metal surfaces have not been so clearly elucidated because of the strong interaction between the adsorbed species and metal atoms, and the rapid electronic decay processes. There are, however, increasing evidences that nonthermal photochemical processes play important roles in certain gas-solid systems where the solids absorb the laser photons.

An important effect of laser irradiation on solid surfaces involves the desorption of adsorbed species, namely, the laser-stimulated desorption. This can be accomplished by means of surface heating or resonant vibrational and electronic excitation of the adsorbate-surface complexes. The subject has been reviewed recently /13/. Briefly, in laser-induced thermal desorption (LITD), surface heating can result from the direct lattice phonon excitation or the initial substrate electronic excitation, e.g. via the electron hole pairs, which subsequently decays to phonon bath before desorption occurs. The unique features of LITD are the rapid and the large range of heating rates allowing one to examine the desorption kinetics over a wide dynamic range. In addition, operation with short laser pulses can facilitate timeresolved studies and provide a means to desorb surface intermediate species not detectable by other methods. Indeed, LITD has been successfully employed to study surface diffusion of CO on Cu /14/, and to determine reaction products in Si/ XeF<sub>2</sub> reaction /15/ and methanol decomposition on Ni /16/.

In resonantly stimulated photodesorption, one can use IR lasers to excite surface vibratinal modes (IRPD) or UV-visible lasers to promote electronic excitation (UVPD). In IRPD, the quantum yields are generally very low and the desorption rates are determined by the IR absorption cross sections. There are no clear vibrational mode enhancement or isotope selectivity in photodesorption yields /17/ because of resonant heating and electronic damping effects /18/. In UVPD, careful systematic studies on well-characterized surfaces are still few. A recent experiment showed that CH<sub>2</sub>Br adsorbed on LiF could be efficiently photodissociated and the fragments could be desorbed by an excimer laser /19/. Furthermore, the photogenerated CH, radicals possessed relatively high kinetic energies apparently because part of the electronic energy after breaking of the CH2-Br bond was transformed into the translational energy of the desorbing fragments. Similar effects involving photoexcitation into the lowest adsorbate antibonding state was observed in CH\_12/ Al<sub>2</sub>O<sub>3</sub> system /20/. There were also reports of CO<sub>2</sub> and  ${\rm H_{2}O}$  desorption from oxide semiconductors induced by band gap excitation with UV light /21/. Other UVPD studies have been related mainly to photochemical etching further discussed below.

In addition to etching, laser-induced vapor deposition (LCVD) has been extensively investigated and a few reviews are available /3,22/. Basically a laser beam is used to decompose gaseous or condensed molecules and induce part of the photofragments to deposit on a solid surface. By this approach, many metals, insulators and semiconductors have been deposited on various substrates. The deposition reaction can be initiated pyrolytically or photolytically or a combination of both. While for the pyrolytic LCVD, the reaction kinetics is controlled by the local heating of the substrate and the newly formed film, direct photodecomposition of molecules in the gaseous and/or adsorbed phases is required for the photolytically activated LCVD, at least in the initial

phase of the deposition. Although there are many LCVD reports on the deposition phenomenon in the last five years, the microscopic mechanisms and the nucleation processes, whether it is initiated by the photothermal or the photolytical means are not at all clear, in particular, in the initial stage of the film growth.

#### 3. Photochemical Etching of Solids

A surface etching reaction can be enhanced by photoexcitation in gas phase and/or in the adsorbed phase. For practical purposes, the most effective etching reactions are achieved by direct photon irradiation on solid surfaces exposed to reactive gases. The subject has been reviewed recently /2,15,23/ and a brief summary of recent studies is given in Table 1. Mechanistically, the characteristics of the surface etching reactions can be divided into three classes, namely, the spontaneous etching, the passive and the diffusive reaction systems. In a spontaneous etching system, the reaction can take place in the absence of radiation and a photon beam can enhance the reaction rate. In a passive reaction system, the reaction results in the formation of a thin passivated layer and in a diffusive reaction, the reactant not only can be adsorbed on the surface but also can penetrate quite deeply into the bulk of the solid. In these two classes of reactions, surface etching does not occur without thermal activation or external radiation.

An example for the spontaneous etching system is silicon exposed to XeF2. Its reaction rate can be greatly enhanced by visible and IR lasers /2,12, 15,24/. A short visible light pulse can induce desorption of surface intermediate species such as SiF and SiF2. Time-of-flight measurements showed that the translational temperatures of the photodesorbed SiF<sub>x</sub> (x  $\leq$  3) could be substantially lower than the calculated surface temperature raised by the laser pulse /15/. Also, in the dark (thermal) reaction /25/ and the cw Ar laser enhanced reaction /12/,  $SiF_4$  was found to be the major reaction product. In contrast, less F-coordinated species and even Si atoms were detected to be the dominant desorption species when excited by a UV or visible laser pulse. A field-assisted  $\ensuremath{\mathsf{F}}^-$  anion

penetration into the subsurface region of Si was suggested /26/ to be the mechanism for Si-fluorine reaction. In analogy, a field-enhanced effect could also be important in the photon-enhanced etching reaction, although a mechanism involving the direct participation of electrons and holes generated by the photon irradiation was also proposed /12/.

Unlike XeF2, Cl2 does not etch a pure Si spontaneously at 25°C in the absence of radiation even though Cl, can dissociatively chemisorb on Si. The reaction rate decreases drastically after the formation of a thin chemisorption layer. It is thus a passive reaction system. Irradiation by UV lasers on silicon can induce efficient etching of the solid /7,27,28/. It was further found /27/ that the n-type Si could even be spontaneously etched by Cl atoms generated by Cl<sub>2</sub> photolysis. Also, the photoinduced etch rate on the n-type Si decreased with increasing sheet resistance, whereas the p-type material showed the opposite effect. The results were interpreted also in terms of the field-assisted mechanism /26/. Namely, the reaction rate could increase with the electron density in the conduction band which led to the formation of Cl anions. The anions could subsequently penetrate into the subsurface region of Si and thereby facilitate the formation of etching products. This lattice penetration was assisted by the surface electric field established across the chlorinated surface layer.

The diffusive reaction can be best illustrated in the reaction of Ag and Cu with Cl<sub>2</sub> /28-30/. In these systems, Cl anions penetrate quite deeply into the bulk of the metals. Chlorine penetration can weaken the metal-metal bonds even at relatively low Cl<sub>2</sub> exposures, and can thus facilitate the efficient etching of the metal by UV or visible laser pulses. When a Cu surface containing some chlorine, e.g. with the average surface Cl concentration in the form of CuCl, /29/ of about 20 % (x = 0.2), was irradiated by a UV or visible light pulse, desorption of Cu<sub>3</sub>Cl<sub>3</sub>, Cu<sub>2</sub>Cl<sub>3</sub>, Cu<sub>2</sub>Cl, etc. molecular species and Cu atoms, in addition to some Cl were detected /30/. The velocities of the photodesorbed particles were generally very high and could not be fitted into Boltzmann dis-

tributions. The mass distribution of desorbed species also differed drastically from that obtained by the thermal evaporation of a solid CuCl. In fact, laser irradiation on a solid CuCl produced a very different time-of-flight spectrum. Furthermore, plasma formation and ion emission were always detected along with the ejection of neutral particles from the lase-irradiated solid CuCl /30/. Apparently for a solid CuCl, photon irradiation can promote "photon-sputtering" involving the formation of a dense electron- hole plasma. As suggested by Itoh and Nakayama /31/ in other systems, multiple-hole states near the surface could be generated in a dense e-hole plasma. The nonradiative e-hole recombinations could energize surface atoms and induce desorption of particles with kinetic energies much higher than that expected from the surface temperature. Overall, however, the photochemical etching behavior of the Cu/Cl<sub>2</sub> system is very different from the photetching or photoablation of a solid CuCl. Both systems exhibit electronic excitation effects, although the exact mechanism for the metal-chlorine system remains to be further elucidated.

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#### References

- / 1/ T. J. Chuang, Surf. Sci. Reports <u>3</u>, 1-105 (1983); also Surf. Sci. (1986, in press).
- / 2/ T. J. Chuang, J. Vac. Sci. Technol. <u>21</u>, 798 (1982).
- / 3/ D. J. Ehrlich and J. Y. Tsao, J. Vac. Sci. Technol. <u>B1</u>, 969 (1983); R. M. Osgood, Jr., Ann. Rev. Phys. Chem. <u>34</u>, 77 (1983).
- / 4/ T. J. Chuang, J. Chem. Phys. <u>74</u>, 1453 (1981) and 72, 6303 (1980).
- / 5/ J. I. Steinfeld, T. G. Anderson, C. Reiser, D. R. Denison, L. D. Hartsough and J. R. Hollahan, J. Electrochem. Soc. <u>127</u>, 514 (1980).
- / 6/ M. Hanabusa, A. Namiki and K. Yoshihara, Appl. Phys. Lett. 35, 626 (1979).
- / 7/ D. J. Ehrlich, R. M. Osgood, Jr., and T. F. Deutsch, Appl. Phys. Lett. <u>38</u>, 1018 (1981).

- / 9/ D. J. Ehrlich, R. M. Osgood, Jr., and T. F. Deutsch, Appl. Phys. Lett. <u>38</u>, 946 (1981).
- /10/ S. A. Schafer and S. A. Lyon, J. Vac. Sci. Technol. <u>21</u>, 422 (1982), and <u>19</u>, 494 (1981); E. M. Young and W. A. Tiller, Appl. Phys. Lett. <u>42</u>, 63 (1983).
- /11/ M. Matsuura, M. Ishida, A. Suzuki and K.
  Hara, Jap. J. Appl. Phys. <u>20</u>, L726 (1981);
  W. G. Petro, I. Hino, S. Eglash, I. Lindau,
  C. Y. Su and W. E. Spicer, J. Vac. Sci.
  Technol. <u>21</u>, 405 (1982).
- /12/ F. A. Houle, J. Chem. Phys. <u>79</u>, 4237 (1983) and <u>80</u>, 4851 (1984).
- /13/ T. J. Chuang, J. Vac. Sci. Technol. <u>B3</u>, 1408 (1985).
- /14/ R. Viswanathan, D. R. Burgess, Jr., P. C. Stair and E. Weitz, J. Vac. Sci. Technol. <u>20</u>, 605 (1982).
- /15/ T. J. Chuang, I. Hussla and W. Sesselmann, in Laser Processing and Diagnostics, edited by D. Bäuerle (Springer, Heidelberg, 1984), p. 300.
- /16/ R. B. Hall and A. M. DeSantolo, Surf. Sci. <u>137</u>, 421 (1984); also R. B. Hall, A. M. DeSantolo and S. J. Bares, Surf. Sci. <u>161</u>, L533 (1985).
- /17/ T. J. Chuang, H. Seki and I. Hussla, Surf. Sci. <u>158</u>, 525 (1985).
- /18/ I. Hussla, H. Seki, T. J. Chuang, Z. W. Gortel, H. J. Kreuzer and P. Piercy, Phys. Rev. <u>B32</u>, 3489 (1985).
- /19/ E. B. D. Bourdon, J. P. Cowin, I. Harrison, J. C. Polanyi, J. Segner, C. D. Stanners and P. A. Young, J. Phys. Chem. <u>88</u>, 6100 (1984).
- /20/ K. Domen and T. J. Chuang, (to be published) .
- /21/ T. Kawai and T. Sakata, Chem. Phys. Lett. 69, 33 (1980); N. Van Hieu and D. Lichtman, Surf. Sci. 103, 535 (1981).
- /22/ D. Bäuerle, in Laser Processing and Diagnostics, edited by D. Bäuerle (Springer, Heidelberg, 1984), p. 166.
- /23/ T. J. Chuang, Mat. Res. Soc. Symp. Proc. 17, 45 (1983); ibid., 29, 185 (1984).

- /24/ T. J. Chuang, J. Chem. Phys. <u>74</u>, 1461 (1931), also J. Vac. Sci. Technol. <u>18</u>, 638 (1931).
- /25/ Y. Y. Tu, T. J. Chuang and H. F. Winters, Phys. Rev. <u>B23</u>, 823 (1981); H. F. Winters and F. A. Houle, J. Appl. Phys. <u>54</u>, 1218 (1983).
- /26/ H. F. Winters, J. W. Coburn and T. J. Chuang, J. Vac. Sci. Technol. <u>B1</u>, 469 (1983).
- /27/ T. Arikado, M. Sekine, H. Okano and Y. Horiike, Mat. Res. Soc. Symp. Proc. 29, 167 (1984).
- /28/ W. Sesselmann and T. J. Chuang, J. Vac. Sci. Technol. <u>B3</u>, 1507 (1985); also Surf. Sci. 162, 1007 (1985).
- /29/ W. Sesselmann and T. J. Chuang, Surf. Sci. (1986, to be published).
- /30/ W. Sesselmann, E. E. Marinero and T. J. Chuang, Appl. Phys. A (to be published).
- /31/ N. Itoh and T. Nakayama, Phys. Lett. <u>A92</u>, 471 (1982); T. Nakayama, M. Okigawa and N. Itoh, Nucl. Instr. Meth. Phys. Res. <u>B1</u>, 301 (1984).
- /32/ I. M. Beterov, V. P. Chebotaev, N. I. Yushina and B. Ya. Yurshin, Sov. J. Quantum Electron. 8, 1310 (1978).
- /33/ G. P. Davis, C. A. Moore and R. A. Gottscho, J. Appl. Phys. 56, 1808 (1984).
- /34/ D. J. Ehrlich, R. M. Osgood, Jr., and T. F. Deutsch, Appl. Phys. Lett. 36, 698 (1980).
- /35/ C. I. H. Ashby, Appl. Phys. Lett. 45, 892 (1984); 46, 752 (1985).
- /36/ L. L. Sveshnikova, V. I. Donin and S. M. Repinskii, Sov. Tech. Phys. Lett. <u>3</u>, 223 (1977).
- /37/ G. L. Loper and M. D. Tabat, Appl. Phys. Lett. 46, 654 (1985).
- /38/ K. Daree and W. Kaiser, Glass Technol. <u>18</u>, 19 (1977).
- /39/ S. Yokoyama, Y. Yamakage and M. Hirose, Appl. Phys. Lett. <u>47</u>, 389 (1985); M. Hirose, S. Yokoyama and Y. Yamakage, J. Vac. Sci. Technol. <u>B3</u>, 1445 (1985).
- /40/ J. H. Brannon, J. Phys. Chem. <u>90</u>, 1784 (1986).
- /41/ G. L. Loper and M. D. Tabat, SPIE 459, 121
  (1984).

/42/ M. Takai, H. Nakai, J. Tsuchimoto, J. Tokuda, T. Minamisono, K. Gamo and S. Namba, in Laser Processing and Diagnostics, ed. by D. Bäuerle (Springer, Heidelberg, 1984), p. 315.

Solid	Gas	Laser	Optical Configuration	Etch Rate or Etch Yield/Pulse	Spot Size/ Resolution	References
Ge	Br <sub>2</sub>	Ar (cw)	focused //	∿10 <sup>-3</sup> µm/sec	(NA)	(32)
Ge	Br <sub>2</sub>	Dye (pulsed)	focused L	0.2 Å/pulse	(NA)	(33)
	CH_ Br					
GaAs	CH3CI	Ar	focused	$10^{-3} \mu m/sec$	1.5 μm	(34)
InP	CF3I	(cw)	1			
GaAs	HCl/He plasma	Ar (cw)	unfocused L	$6 \times 10^{-4} \mu m/sec$	∿100 µm	(35)
GaAs	<sup>Cl</sup> 2, <sup>CCl</sup> 4	Ar (cw)	focused	∿2 µm/sec	∿1 µm	(42)
Si	Cl <sub>2</sub>	XeCl (pulsed)	unfocused L	(NA)	∿1 µm	(27)
Si	Br <sub>2</sub>	Ar (cw)	focused //	<u>&lt;</u> 10 <sup>-4</sup> µm/sec	(NA)	(36)
	Cl <sub>2</sub>	Ar	focused			
Si	HCl	(cw)	1	0.02 ∿ 10 µm/sec	5 µm	(7)
		co <sub>2</sub>	unfocused			
Si	SF6	(pulsed)	- <b>1</b>	1.2 Å/pulse	(NA)	(4)
		co,	focused			
Si	SF6	(pulsed)	11	0.05 Å/pulse	(NA)	(4)
		co,	unfocused			1
Si	XeF <sub>2</sub>	(pulsed)	Ŧ	0.6 Å /pulse	(NA)	(24)
Si	XeF <sub>2</sub>	Ar (cw)	unfocused L	$6 \times 10^{-4} \mu m/sec$	(NA)	(12)
Si	COF <sub>2</sub>	ArF (pulsed)	unfocused +	0.13 Å/pulse	(NA)	(37)
sio <sub>2</sub>	HF	CO <sub>2</sub> (cw)	focused L	0.05 µm/sec	∿100 µm	(38)
	CF <sub>3</sub> Br	co,	focused			
sio <sub>2</sub>	CDF3	(pulsed)	11	0.3 Å/pulse	∿200 µm	(5)
sio <sub>2</sub>	Cl <sub>2</sub>	Ar (cw)	focused L	$3 \times 10^{-4} \mu m/sec$	50∿ 80 µm	(8)
sio <sub>2</sub>	NF3/H2	ArF (pulsed)	unfocused	0.02 Å/pulse	(NA)	(39)
Sio,	CF <sub>2</sub> Br <sub>2</sub>	KrF	unfocused	0.6 Å/pulse	(NA)	(40)
2	C <sub>2</sub> F <sub>4</sub>	(pulsed)	Ľ	in an analog a second diggenology.gette		
sio <sub>2</sub>	CF2Cl2	KrF (pulsed)	unfocused	0.13 Å/pulse	(NA)	(41)

## Table 1

Summary of recent studies on laser-enhanced chemical etching of solids by gases

Mo,Ti	NF <sub>3</sub>	ArF (pulsed)	unfocused ±	0.3 Å/pulse	(NA)	(41)
Al	Cl <sub>2</sub>	XeCl (pulsed)	unfocused L	30 Å/pulse	(NA)	(28)
Ag,Mo	Cl <sub>2</sub>	N <sub>2</sub> (pulsed)	focused L	3 Å/pulse	(NA)	(28)
Cu	Cl <sub>2</sub>	Nd:YAG (0.53+0.35µ (pulsed)	focused m) <b>±</b>	(NA)	(NA)	(30)
		CO.	unfocused			
Ta	SF <sub>6</sub>	(pulsed)	1	2.6 Å/pulse	(NA)	(24)
		CO	unfocused			
Та	XeF <sub>2</sub>	(pulsed)	Ŧ	0.4 Å/pulse	(NA)	(24)
		co	unfocused			
Те	XeF <sub>2</sub>	(pulsed)	T	10 Å/pulse	0.5 µm	(8)
Ni(80%)	SF, CF	Ar	focused			
Fe(20%)	ccl <sub>4</sub> ,cl <sub>2</sub>	(cw)	Ŧ	0.1 µm/sec	80 µm	(23)
Ni,Fe	Cl <sub>2</sub>	Na	focused	2 Å/pulse	(NA)	(28)
	2	(pulsed)	1			÷6
		Ar	focused			
TiC-	CCl <sub>4</sub>	(cw)	Ŧ	0.1 µm/sec	10-100 µm	
Al 203	SF <sub>6</sub>	Nd:YAG (pulsed)	focused	$5 \times 10^{-3} \mu m/pulse$	10-100 µm	(23)

Table 1 (continued)

Notes: (1) // and -, the laser beam incident either parallel (//) or perpendicular (-) to the solid surfaces.

(2) NA, data either not available or unspecified.

