

LOW PRESSURE PLASMA DIAGNOSTICS BY CARS AND OTHER TECHNIQUES

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ABSTRACT

Within the past several years, intensive research activities relating amorphous-silicon technology have stimulated plasma-chemical-vapor-deposition (plasma-CVD) diagnostics by laser-spectroscopic techniques. Among them, coherent anti-Stokes Raman spectroscopy (CARS) has attracted much attention because of its great success in combustion diagnostics, and has been employed for low-pressure-plasma studies. Gas-phase species such as SiH_4 , H_2 , Si_2H_6 , SiH_2 , and GeH_4 have been detected, time dependences of their concentration and spatial profiles of their concentration and rotational temperature have been determined, and the gas-phase mechanisms have been discussed. This talk will employ those results as examples, and discuss (1) the potential of CARS for gas-phase analysis in CVD (including (i) what species are monitored, (ii) what information is obtained, and (iii) what are the advantages and limitations), and (2) some other diagnostic techniques that provide additional information for better understandings of CVD mechanisms.

INTRODUCTION

Diamond synthesis from the gas phase has attracted much attention in science and applications (1-7). There are a lot of techniques to produce carbon thin films, and they are divided into chemical vapor deposition (CVD), and physical vapor deposition (PVD). In CVD methods, source gas molecules containing carbon atoms are activated thermally, optically, or by electron collision, and molecular fragments are created. They then diffuse in the gas phase to the substrate surface to feed the surface processes that grow carbon thin films. In PVD methods, particles that contain carbon atoms are fed to the surface. Sputtering and ion-beam deposition are classified in this category.

There are a lot of applications of carbon thin films. Among them, one of the most attractive ones is the micro-electronic applications. Diamond has a high resistivity, thermal conductivity, transparency, and wide band-gap width. It shows semiconducting characteristics when some impurities are doped. These features suggest that thin film diamond will possibly be used as an important material for insulator of field-effect devices, photoconductors, high-temperature devices, short-wavelength light-emitting devices, and radiation resistive devices. In order to realize those electronic applications, development of low-temperature fabrication technology with less damage to the substrate and high controllability of structure and characteristics is required very much.

Thin film carbon has a lot of structural types such as diamond, diamond-like carbon, i-carbon, amorphous carbon, and graphite. Relationships between the film structure and the fabrication methods as well as the operating conditions are partly

known empirically. Understanding of the gas-phase and surface mechanisms that govern those relationships will lead to superior fabrication technology with high controllability. And the first step to such understanding is the observation of the gas phase and surface.

Within the past several years, amorphous silicon related materials have been investigated intensively because of their potential for applications. At present, they are mostly fabricated by plasma-chemical-vapor deposition (plasma-CVD), and their properties are sensitive to the plasma operating conditions. Therefore, the research activities relating the amorphous-silicon technology have stimulated plasma-CVD diagnostics, especially those by laser spectroscopic techniques. Gas-phase process diagnostics by laser spectroscopy have several advantages and enable non-intrusive in-situ observation.

Among them, coherent anti-Stokes Raman spectroscopy (CARS) has attracted much attention because of its great success in combustion diagnostics (8), and has been employed for low-pressure-plasma studies (9). Gas-phase species such as SiH_4 , H_2 , Si_2H_6 , SiH_2 , and GeH_4 have been detected, time dependences of their concentration and spatial profiles of their concentration and rotational temperature have been determined, and the gas-phase mechanisms have been discussed (9-14).

In addition to CARS, laser induced fluorescence (LIF) was employed, and gas-phase species such as Si and Ge were measured. Optical emission spectroscopy, which is, in fact, not a laser spectroscopy, was also employed, and Si, SiH , H_2 , H, and Ge in their electronically ground states were measured. It has been demonstrated that all those techniques provide information about different sets of species to one another, and therefore, more information is obtained by combining several techniques (13,14).

Low-temperature CVD processes such as plasma-CVD for amorphous-silicon-related materials are preferred for micro-electronic applications to PVD and thermal-CVD processes because of their film growth at lower temperature with less damages to the substrate. Although the crystalline size is different from that of thin film diamond, microcrystalline silicon ($\mu\text{c-Si}$) film is more like to it than amorphous silicon (a-Si) film. The deposition conditions for $\mu\text{c-Si}$ is higher in excitation power and hydrogen dilution than those for a-Si. This tendency is almost the same to the deposition conditions for thin film diamond compared with those for carbon films of other structures. Another similarities are their low growth rates, which sometimes are serious problems for applications.

Once the gas-phase profiles of specie concentration and temperature were measured and understood, the efforts of the process-diagnostic research have come to be directed to some key issues in the deposition processes. They are: (1) the effects of ion bombardment to the surface (15), (2) the roles of hydrogen in the gas-phase and at the surface, (3) the dominant species that contribute to the deposition, and (4) the role of O and N atoms to the growth rate (5). Recently, methyl radical CH_3 , which was long considered as the dominant specie, was experimentally detected by infrared diode laser spectroscopy (16). And atomic hydrogen was detected by laser ionization technique (17). Those are the typical examples of the recent trend in process diagnostic research.

This talk includes (1) our experimental setup for gas-phase process diagnostics, (2) a review of the important results in the diagnostics of plasma-CVD for amorphous-silicon-related materials, (3) potential of the techniques for gas-phase analysis in diamond CVD, and (4) another technique to reveal the key mechanisms.

EXPERIMENTAL

Light Sources

Gas pressure in plasma CVD is much lower than the atmospheric pressure, and therefore, high power is required for the CARS light sources. Furthermore, tunable ultraviolet light is necessary for LIF of Si and Ge, and it has to be generated by frequency mixing laser lights. Those are the requirements for a high power laser as the light source. In the experiment, Q-switched Nd:YAG laser (Quanta-Ray, Model DCR-2A) system with an amplifier and an second harmonics generator was used to produce 532 nm second harmonics with 2 ns pulse width and 350 mJ pulse energy, as well as the fundamental 1064 nm laser light. Some part of the 532 nm laser light was used to pump the pulsed dye laser (Quanta-Ray, Model PDL-1) with an amplifier and a wavelength control interface (Quanta-Ray, Model MCI-1). To obtain tunable ultraviolet light for LIF measurements, the dye laser light was frequency doubled and mixed with the fundamental 1064 nm light from the Nd:YAG laser by using the wavelength extender (Quanta-Ray, Model WEX-1). Another dye laser (Quanta-Ray, Model PDL-2) was used to obtain tunable visible light.

All those laser systems were set on a long optical bench, and mirrors and beam splitters were arranged so as to generate laser lights necessary to CARS, LIF and another technique. For CARS, 545-690 nm dye laser light and 532 nm Nd:YAG laser second harmonics were collinearly collimated using a dichroic mirror and then introduced into the plasma-CVD chamber through a focusing lens. And for LIF, 245-280 nm tunable ultraviolet light was generated and introduced into the chamber through quartz optics.

Plasma-CVD Chamber

A specially designed capacitively-coupled diode-type radio-frequency (13.56 MHz) plasma-CVD chamber equipped with three optical window ports was used. The diameters of cathode and anode were 90 and 110 mm, respectively, and their separation was 30-40 mm (variable). The chamber wall was 250 mm apart from the center, and the optical ports were 100 mm long and had quartz windows of 100 mm in diameter at the ends. The chamber was pre-evacuated to 10^{-5} Pa by a 6-inch oil-diffusion pump, and then the valve was closed, the reactant gas was introduced, and was pumped out with a root pump to keep the pressure typically at 10-100 Pa.

Detection Optics

Detection optics for CARS were designed to separate CARS signal light from laser lights, plasma emission, and ambient lights. Mixed beams of lasers and CARS signal were collimated using a lens, and laser lights were separated away using two

dichroic filters, and 1-m double monochromator (Jobin Yvon, Model U1000). Non-resonant CARS signal was rejected using an analyzer, while polarizers were placed in the light source optics to constitute the polarization CARS configuration (18). The CARS signal was detected by an intensified photo-diode array detector (Princeton Applied Research, Model 1420).

Detection optics for LIF and OES were designed to collect the emitted light from gas-phase species. Two quartz lenses of 350 mm focal length and 60 mm diameter were used to collect the light and introduce it into the entrance slit of 32 cm grating monochromator (Jobin Yvon, Model HR320). The signal light was detected by a photomultiplier (HAMAMATSU, Model R292).

Control and Data Acquisition

The Nd:YAG laser was operated at 10 shots per second, and the CARS signal was accumulated at each dye laser wavelength for 10-100 laser shots, and then the dye laser wavelength was changed. Plasma conditions were set manually, and the measuring point was changed by moving the plasma-CVD chamber. The LIF signal from the photomultiplier was accumulated in a boxcar integrator (Princeton Applied Research, Model 4420) with the laser shots as the trigger pulses, and the noises that did not coincide with the laser shots were removed.

PLASMA-CVD FOR AMORPHOUS SILICON RELATED MATERIALS

Temperature Profile

Silane (SiH_4) molecule is abundant in the gas phase of most of the plasma-CVD for amorphous-silicon-related materials. Therefore, temperature determination from SiH_4 CARS signal was performed. A simple equation for SiH_4 CARS spectrum:

$$(\sum_j \exp[-hcBJ(J+1)/kT] \exp\{-[\delta v - v_0 - \Delta BcJ(J+1)]^2 / (\Delta v)^2\})^2 \quad (1)$$

was assumed and the spectral shapes for different values of rotational temperature T were calculated (12). Then the measured CARS spectra were compared with those calculated curves to find the best fitted one, from which the values of rotational temperature were obtained. From the result, the effects of the substrate heating and radio-frequency discharge to the gas-phase temperature were discussed.

Hydrogen (H_2) molecule is abundant in the gas phase not only of the plasma-CVD for amorphous-silicon-related materials but also many other CVD processes. It is known in diamond CVD that heavily diluting the source gas molecule with hydrogen is very important for obtaining diamond structure. Both the ro-vibrational and pure rotational CARS spectra of H_2 show a series of peaks that corresponds to a series of the rotational quantum states (19-21). That is due to the large values of the rotational constants of H_2 molecule consisting of light H atoms. From the ratio of the CARS signal peak intensities, distribution within those rotational states, and therefore, the rotational temperature is obtained. The pure rotational CARS signal is about 100 X stronger in intensity than the ro-vibrational signal, and suited for low-pressure plasma-CVD

diagnostics. The relative peak intensities are given by the square of the non-linear electric susceptibility $\chi^{(3)}(J,J+2)$, which is written as (20),

$$\chi^{(3)}(J,J+2) = N(J+1)(J+2)[X(J,T)-X(J+2,T)] / Q(T)(2J+3) \quad (2)$$

$$X(J,T) = g_J \exp[-E(J)/kT] \quad (3)$$

$$Q(T) = \sum g_J(2J+1) \exp[-E(J,v)/kT] \quad (4)$$

$$E(J,v) = E_v^0 + B_v J(J+1) + D_v J^2(J+1)^2 + H_v J^3(J+1)^3 \quad (5)$$

By measuring the hydrogen CARS spectra from one point to another, the temperature profile in the gas phase was determined (20). From the results, it was concluded that the gas-phase temperature is mostly determined by the substrate and chamber-wall temperatures and is little affected by the other plasma operating conditions within the range used for amorphous-silicon deposition. That is consistent with the fact that the gas-phase temperature relaxation time determined by the ratio of the heat capacity to thermal conductivity is much shorter than the gas residence time in the chamber. And the gas-phase temperature in the vicinity of the film-growing surface agreed with the surface temperature measured with a thermocouple.

Concentration Profile

The concentration of molecule is determined from the CARS signal intensity by using the quadratic dependence of the CARS signal intensity I_{CARS} to the concentration $[M]$ of the resonant molecule M:

$$I_{\text{CARS}} \propto |\chi^{(3)}|^2 \propto [M]^2 \quad (6)$$

By measuring the CARS signal from one point to another, the concentration profile is obtained. The absolute value of the molecular concentration is determined by using the gas of known concentration for calibration. OES signal also represents the relative concentration of the species that emit the photons when the emission efficiency is constant and the absorption of the emitted photons by other species is neglected. In addition to the necessary conditions for OES signal to be a measure of specie concentration, if the excitation light is not attenuated much along its path, the LIF signal is a measure of the specie concentration.

The concentration profiles of SiH_4 , Si, and Si^+ were measured between the cathode and anode along the central axis, and much different profiles were obtained among those species. Si concentration had a two distinct peaks at about 10 mm from the cathode and anode, while SiH_4 concentration changed more gradually and was almost constant in the discharge volume except the sheath regions (14). The result was interpreted that a lot of Si atoms are created by electron collision in the regions where electron energy is high. The highly energetic electrons are created by the acceleration of secondary emitted electrons from the electrodes by the sheath electric fields. SiH_4

molecule, on the other hand, is dissociated or excited even by electrons with lower kinetic energy, thus more gradual change in the discharge region is realized.

The concentration profiles of SiH_4 and GeH_4 in a plane parallel to the electrode surface were also measured, and gradual concentration changes of the both molecules toward the radial direction were observed (13). The result was interpreted in terms of dissociation and excitation of the source gas molecules supplied from outside of the discharge by molecular diffusion.

Transient Behavior

Concentrations of SiH_4 and Si_2H_6 were measured as functions of time after the discharges were switched on in a closed discharge chamber (11). The concentrations of source gas molecules decreased exponentially with time, and the decay time constants were obtained from the slope of the concentration plotted semi-logarithmically against time. From the time constants, the average loss rates were calculated and their dependences on the gas pressure and discharge power were studied. In Si_2H_6 discharges, SiH_4 molecule was observed, and the time dependence of its concentration was studied. The result was interpreted in terms of the average creation rate, and compared with the average loss rate to discuss the formation mechanism of SiH_4 in Si_2H_6 discharges.

Effect of Hydrogen Dilution

Effect of Hydrogen dilution on the OES and LIF signals of Si^* , Ge^* , Si, and Ge was studied (13). Emission signal from Ge^* from GeH_4 discharge decreased very much with dilution of the source gas GeH_4 with H_2 , while emission signal from Si^* did not change very much with H_2 dilution. Si and Ge atoms in their electronically ground states measured by LIF changed like their emissive species with H_2 dilution. The results were interpreted in terms of the gas-phase mechanisms with H_2 dilution.

DIAMOND CVD

As the first step for process diagnostics, measurements of temperature and specie concentration profiles will provide much information. The laser spectroscopic process-diagnostic techniques demonstrated in plasma CVD for amorphous-silicon-related materials are applicable to other CVD systems if some suitable optical windows are equipped. The arguments are what species are detected, what the detection limit is, and what information is obtained. The situation seems better for CARS measurements in diamond CVD processes, since the gas pressure is usually higher than that in plasma-CVD for amorphous-silicon-related materials. Hydrogen (H_2), methane (CH_4), and some other carbon-containing molecules will be detected by CARS, and their concentration profiles will be measured. Temperature measurement by pure-rotational CARS signal of H_2 will also be practical, and temperature profile will be obtained. As in the case of plasma CVD for amorphous-silicon-related materials, species detected by LIF will be limited to some molecular fragments, but LIF will still add information to

CARS data. Thus the first step of the diamond-CVD diagnostics will be fulfilled with the techniques used in the plasma-CVD diagnostics.

ANOTHER TECHNIQUE

What should be carried out at the next stage is to focus on the key issues: (1) the role of hydrogen, (2) the dominant species contributing to the film growth, (3) the effects of ion bombardment, and (4) the effects of O and N. For that purpose the detection of hydrogen atom by resonance-enhanced multiphoton laser-induced-fluorescence experiment was planned and is now in progress. That method is similar to the resonance-enhanced multiphoton ionization technique (17) but promises the detection of H even in the plasma CVD environment.

SUMMARY

Laser-spectroscopic gas-phase process diagnostic techniques such as CARS and LIF have been demonstrated in the plasma CVD for amorphous-silicon-related materials. Gas-phase profiles of specie concentration as well as temperature were measured in-situ non-intrusively, and the results were interpreted in terms of gas-phase kinetics. Those techniques will be applicable to other CVD processes, especially those for diamond thin films.

Process diagnostics have come to the stage where the direct observations of the key issues in the processes are strongly emphasized. Understanding of the key mechanisms that determine the growth rate, structure, and properties of thin films is very important. The processes occurring at the film growing surface were mentioned little in this talk, but it plays the other important part in the mechanisms, and should be studied extensively.

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REFERENCES

- (1) Angus, W.G., Will, H.A., and Stanko, W.S.: *J. Appl. Phys.*, 39 (1968) 2915.
- (2) Spitsyn, B.V., Boulov, L.L., and Derjaguin, B.V.: *J. Cryst. Growth*, 52 (1968) 219.
- (3) Matsumoto, S., Sato, Y., Kamp, M., and Setaka, N.: *Jpn. J. Appl. Phys.*, 21 (1982) L183.
- (4) Sawabe, A. and Inuzuka, T.: *Appl. Phys. Lett.*, 46 (1985) 146.
- (5) Hirose, Y. and Terasawa, Y.: *Jpn. J. Appl. Phys.*, 25 (1986) L519.
- (6) Suzuki, K., Sawabe, Y., Yasuda, H., and Inuzuka, T.: *Appl. Phys. Lett.*, 50 (1987) 728.
- (7) Matsumoto, S., Hono, M., and Kobayashi, T.: *Appl. Phys. Lett.*, 51 (1987) 737.
- (8) Eckbreth, A.C.: *J. Propulsion and Power*, 3 (1987) 210, and references therein.
- (9) Hata, N., Matsuda, A., Tanaka, K., Kajiyama, K., Moro, N., and Sajiki, K.: *Jpn. J. Appl. Phys.*, 22 (1983) L1.
- (10) Hata, N., Matsuda, A., and Tanaka, K.: *J. Non-Cryst. Solids*, 59-60 (1983) 667.
- (11) Hata, N., Matsuda, A., and Tanaka, K.: *Jpn. J. Appl. Phys.*, 25 (1986) 108.
- (12) Hata, N., Matsuda, A., and Tanaka, K.: *J. Appl. Phys.*, 59 (1986) 1872.
- (13) Hata, N., Matsuda, A., and Tanaka, K.: *J. Appl. Phys.*, 61 (1987) 3055.
- (14) Hata, N. and Tanaka, K.: *J. Non-Cryst. Solids*, 77-78 (1985) 777.
- (15) Angus, J.C., Doidl, P., and Domitz, S.: in "Plasma Deposited Thin Films" ed. by Mort, J. and Jansen, F. (CRC Press, Florida, 1986) pp. 89-127.
- (16) Celii, F.G., Pehrsson, P.E., Wang, H.-t., and Butler, J.E.: *Appl. Phys. Lett.*, 52 (1988) 2043.
- (17) Celii, F.G., Pehrsson, F., Wang, T.-t., Nelson, H.H., and Butler, J.E.: in "Extended Abstract of the International Symposium on the Characterization of Diamond" (Tsukuba, Japan, Oct. 27-28, 1988).
- (18) Brakel, R. and Schneider, F.W.: in "Advances in Non-Linear Spectroscopy" ed. by Clark, R.J.H. and Hester, R.E. (John Wiley & Sons, Chichester, 1988) pp. 149-192.
- (19) Pealat, M., Taran, J.P.E., Taillet, J., Bacal, M., and Bruneteau, J. *Appl. Phys.*, 52 (1981) 2687.
- (20) Marowsky, G., Gierulski, A., Dick, B., Sowada, U., and Vehrenkamp, R.: *Appl. Phys.*, B39 (1986) 47.
- (21) Hata, N., Matsuda, A., and Tanaka, K.: in "Symposium Proceedings, 8th International Symposium on Plasma Chemistry" ed. by Akashi, K. and Kinbara, A., (IUPAC, Tokyo, 1987) pp. 500-505.