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Fast deposition of amorphous carbon and silicon layers

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A new plasma deposition technique will be described. In this method a high density and strongly flowing argon plasma is admixed with monomers as CH_4, C_2H_2, SiH_4, etc. Through effective charge transfer and dissociative recombination the ion charge is transferred to the fully dissociated monomer fragments. As the to be deposited particles as C and Si have low ionization potentials they are preferably recharged. The method results in high deposition rates of a-C:H (up to 100 nm/s) and a-Si:H layers (30 nm/s). Properties of the layers will be reviewed and a tentative model for plasma description will be discussed.

1. Introduction

The technology of thin layer deposition has found many important applications varying from small scale objects as (sub)micron technology to large scale ones as corrosion and wear resistant layers, solar cells, membranes, optical coatings etc. [1]. In many of these applications plasma deposition techniques may offer a good alternative, as with plasmas a large material freedom is attainable. A second field of plasma deposition is that of sophisticated materials such as diamond. In particular for large scale applications a high deposition rate is required to make the method also economical. Therefore the question arises whether high deposition rates can be achieved while maintaining the required quality (demands). In the present contribution the results of a new plasma deposition technique, which is based on a separation and thus independent optimization of plasma production and plasma treatment. In this way a plasma ion and radical beam is obtained with a high intensity allowing for high deposition rates. Still major properties of the deposited layers are similar to those produced with more classical plasma deposition techniques.

2. Deposition method

The principle of the plasma beam deposition technique is the separation of plasma production and plasma treatment (fig. 1) [2]. The plasma is produced in a relatively high pressure subatmospheric flowing arc. These so-called thermal plasmas are characterized by high pressure, high power density, high ionization degree and electron density and small lateral dimensions for stable operation. The particular form chosen here is the cascade arc, with three cathodes at the upstream side, cascade plates which serve as an isolating wall and a downstream anode nozzle. Typical ionization degrees are 10% which at pressures of 0.2 atm and temperatures of 10^4 K give electron and thus ion densities of $10^{22}/m^3$ and neutral densities of $10^{23}/m^3$ at the exit nozzle. As a consequence of the high electron density the electrons and heavy particles are thermally coupled with temperatures around 10000 K. The pressure difference which results from the pumping of the deposition chamber accelerates the plasma to a strongly flowing 10% ionized medium with velocities

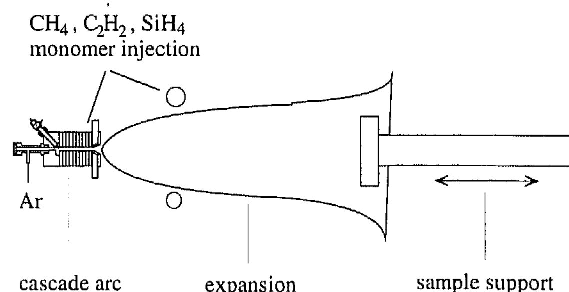

Fig. 1. Outline of the plasma system used in the experiments. The plasma is generated in the cascaded arc and transported towards the substrate by means of a supersonic expansion and a subsonic plasma beam. The monomers can be injected either in the arc or through a ring downstream the expansion.

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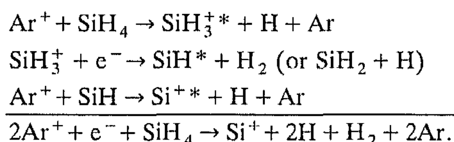
$\sim 10^3$ m/s at the nozzle exit. In some applications hydrogen is admixed to the argon plasma; in a few cm the hydrogen is dissociated and is partially charged by charge exchange. As the thermal plasma is not far from equilibrium the particles with the lowest ionization potential are preferentially charged. The resulting plasma beam in the deposition chamber expands first supersonically, then shocks and finally expands further subsonically.

3. Model considerations

The processes are investigated independently in argon and argon–hydrogen mixtures with Thomson and Rayleigh scattering [3]. The behavior can be understood on the basis of gasdynamic theory. The recombination in atomic gases is weak and the ion fraction is maintained up to the substrate. However, in the presence of hydrogen or hydrogen-containing monomers a substantial recombination is observed which is due to the charge exchange of atomic to molecular ions and subsequent recombination. This fact may have an effect on the deposition results, as will be discussed later. Monomers (CH_4, C_2H_2, SiH_4) are seeded either in the anode nozzle or in a ring in the supersonic expansion. In the expansion the electron temperature decreases to below 0.5 eV. Hence in this scheme the ions form the main active species. The monomers are dissociated, ionized by a sequence of (dissociative) charge exchange, dissociative recombination, etc. A possible reaction scheme for SiH_4 could be [4]:



$$Ar^+ + SiH_4 \rightarrow SiH_3^{+*} + H + Ar$$
$$SiH_3^+ + e^- \rightarrow SiH^* + H_2 \text{ (or } SiH_2 + H)$$
$$Ar^+ + SiH \rightarrow Si^{+*} + H + Ar$$
$$2Ar^+ + e^- + SiH_4 \rightarrow Si^+ + 2H + H_2 + 2Ar.$$

The asterix indicates a probably electronic and/or rovibrational excitation. Actually these processes must be the main source of the atomic and molecular radiation observed, as the electron temperature is too low to allow for significant electron excitation. The analysis of the atomic and molecular emissions allow for determination of atomic ion densities and of the rovibrational temperatures (3000 K typically). From this example it is clear that in this process primarily atomic (ion and radical) fragments result from the plasma interaction with the monomers. This is contrary to the normal plasma deposition techniques (RF or microwaves) in which the fragmentation is far less complete and, e.g., molecular ions are the main ions. At this point it should be remarked that another major difference exists with other methods: the bias potential which is related to the ambipolar fields is remarkably smaller in this method, volts versus tens of volts. As ions are accelerated in this bias potential this leads to 1 to 2 eV ions in this method compared to 30–100 eV in other methods. The fact that notwithstanding these important differences similar properties of the deposited layers are reached will be a second consideration to be discussed later. The width of the expanding plasma beam depends on the pressure. At lower pressures (20–200 Pa) the width and thus the deposition area is 5–10 cm in radius at a distance of 40–80 cm from the nozzle. This is the amorphous layer setting allowing for large area deposition. For crystalline materials higher pressures and higher power fluxes are to be preferred. In this case the distance is varied from a few cm (diamond) to 20 cm (graphite).

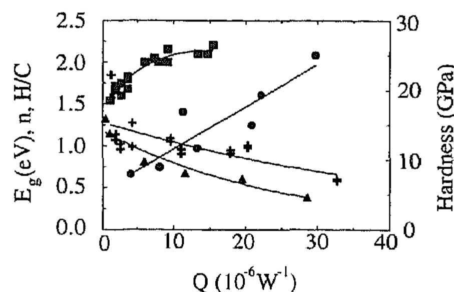


Fig. 2. Plot of some film parameters versus "energy" factor $Q(W^{-1})$. (■) refractive index, (▲) optical band gap, (•) Vickers hardness, (+) H/C ratio.

4. Deposition results

The results on amorphous carbon deposition are summarized in fig. 2. In this figure the index of refraction, measured by He–Ne ellipsometry, the bandgap and C/H ratio measured by nuclear techniques are plotted as a function of the inverse energy factor [2,5,6]. This factor is related to the deposited energy per deposition event. It proves that by variation of the various parameters (arc current, flow, pressure, distance) materials from soft polymeric to hard diamond-like coatings can be obtained. Still the deposition rate can be very large: up to 100 nm/s over areas of 100 cm^2. The fact that the material properties do not differ vastly from those obtained with other methods, despite differences in flux composition and ion energy, points to a thermally determined polymerization process in

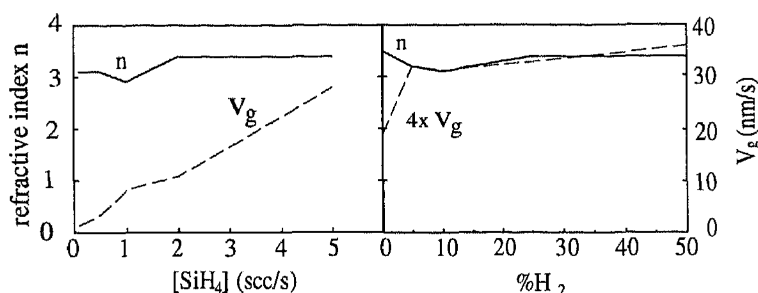


Fig. 3. Refractive index and growth rate of a-Si:H as a function of silane flow rate and H_2/Ar plasma composition.

the gas-adsorbed layer on top of the deposited material. The significant influence of the substrate temperature is another indication. Still more specific kinetic effects as H-atom absorption and a synergetic ion/radical mechanism cannot be excluded at this point. It is clear, however, that low ion energies are permissible, which is a great advantage in avoiding ion-induced damage.

Some results obtained in amorphous hydrogenated silicon deposition are shown in fig. 3 in which the deposition rate, the index of refraction and the bandgap are plotted as a function of SiH_4 admixture (injected in the vessel) and H_2 admixture (injected in the arc). In this case the variations are small except for the linear variation of deposition rate with SiH_4 admixture. The index of refraction is 3.4, the bandgap 1.5 eV (slightly dependent on the method used). The dark/light conductivity ratio is close to 10^{-4}. By infrared absorption experiments it has been established that as a function of time the oxygen content increases, which forms also an explication for the relatively high resistivity of the amorphous material (10^9 instead of 10^7 Ω m for device

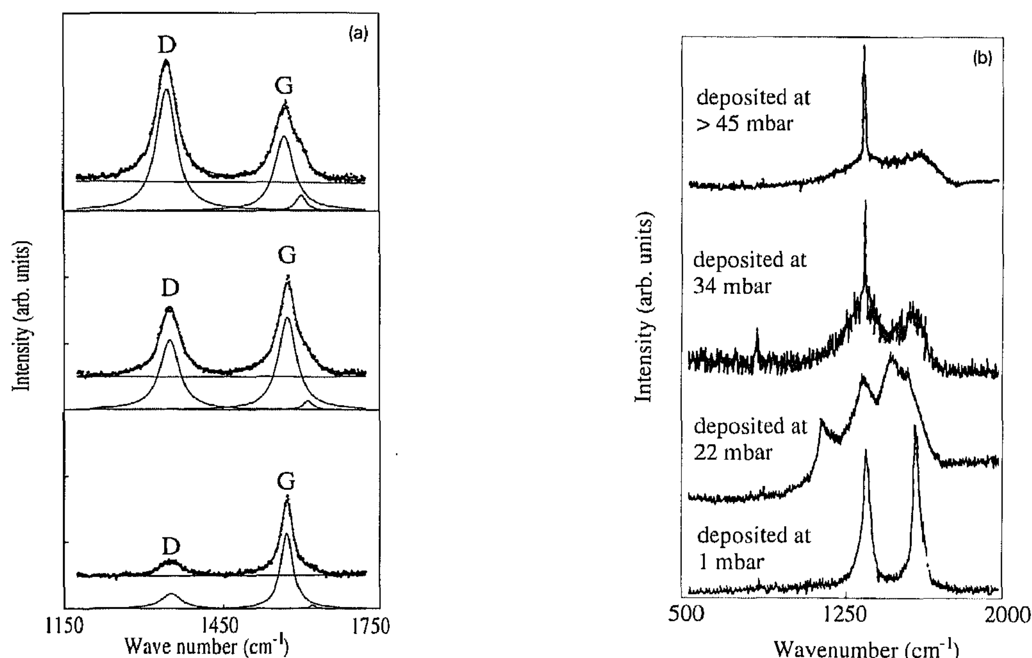


Fig. 4. (a) Effect of increasing hydrogen admixture on Raman spectra of graphite films. From top to bottom the H_2 admixtures are 5, 10, and 20 scc/s; and growth rates 21, 12, and 13 nm/s, respectively. Substrate temperature ~840°C. (b) Raman spectra of diamond films deposited at different pressure levels. In the series of experiments all parameters but the pressure were kept constant.

quality material) [1]. In this case the ion contribution to the deposition is less clear; in combination with the higher substrate temperature ($T \approx 520$ K) it would be an explanation of the small variations of the material quality with conditions.

In the carbon experiment also crystalline materials have been successfully deposited [5,7,8,9]. In this case the substrate has been moved close to the exit nozzle and the substrate temperature is from 1100 (graphite) to 1300 K (diamond). At that position the width of the plasma beam (also depending on the pressure p) is only 2 to 3 cm and the deposition area is correspondingly smaller. The quality of the deposited material varies with the conditions. This is clear from fig. 4a in which the Raman spectrum of graphite deposits is shown as a function of hydrogen admixture. It is evident that with increasing H-admixture the material improves considerably: for the highest admixture the defective graphite peak D has almost disappeared. The growth rate decreases with H-admixture, which is partly due to H-etching but may also be a consequence of ionization loss.

Earlier diamond has been deposited successfully with (large) H_2-admixture and with oxygen admixture [5–7]. Again the material quantities vary significantly with the conditions as is shown in fig. 4b which shows the Raman spectrum for four pressures. From this figure it is evident that the diamond quality increases with ambient pressure. Because the plasma beam narrows with pressure the deposition rate (typically 10 nm/s) increases as well. It is an example of improvement of quality accompanied with increasing growth rate. Hence surface migration may not be the limiting step and it is even possible that plasma recirculation and repeating etching/deposition may replace surface migration.

5. Conclusions

At present it is not possible to obtain a complete picture of the deposition mechanism also because flux composition is not known with sufficient accuracy. However, from the knowledge already acquired it seems that the material can be good for rather wide circumstances. This may point to a thermal growth process in which energy flux to the surfaces and C/H or Si/H abundances play a determining role, rather than the occurrence of specific precursors.

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