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Fast deposition of thin amorphous films using an expanding thermal plasma

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Abstract
The basic elements of expanding plasma beam deposition are explained. The principle of dissociation is discussed and illustrated for an Ar/C_2H_2 plasma. Recent results on high quality a-C:H deposition are discussed. It is demonstrated that quality is not connected to growth rate. Moreover for a-C:H it is shown that quality improves with increasing growth rate.

Introduction

The plasma deposition of thin amorphous films is still an important industrial activity. This is due to the fact that certain properties of these thin films can not be obtained using techniques which do not employ plasmas. In a plasma it is possible to generate deposition precursors at relatively modest power input. This is an advantage as in this way the substrate temperature remains relatively low. Furthermore material combinations can be tuned by varying the plasma properties. Especially during the last decade plasma deposition techniques have been further developed. Both film quality and deposition rate have been improved.

However, certain large scale applications of thin amorphous films are hampered by the relatively large production costs [1,2]. An example is the large scale deposition of corrosion protective amorphous hydrogenated carbon (a-C:H) films on e.g. steel to avoid the environmental polluting electrogalvanization process [2]. It is evident that the production costs of the plasma deposited films in this case should be low to be a real alternative. Fast deposition of both a-Si:H and a-C:H is therefore still an important issue. It becomes even more interesting if the properties of the deposited films can be improved at larger growth rate, results which have been reported in literature for a-Si:H [3]. In this paper we will show this for a-C:H, i.e. the quality of the film in terms of hardness and refractive index increases with growth rate.

This paper deals with an approach of fast deposition of a-C:H using an expanding thermal plasma. Results on the deposition of a-Si:H can be found in Refs. [4,5]. In the next section we will compare this approach with other high density sources. The different properties as electron density and temperature, the ionization and dissociation mechanism of the injected monomer and the influence of transport processes on these mechanism will be dealt with. Finally recent results on the deposition of a-C:H will be presented.

Experiment

In fig. 1 a schematic drawing is given of the plasma used for the fast deposition of a-C:H and a-Si:H. The deposition set-up consists of a thermal plasma, a cascaded arc, an expansion vessel and a substrate holder. Through the plasma source there is a constant flow of usually argon or an argon/hydrogen mixture (typically in the 100 scc/s range) at subatmospheric pressures, which is ionized to a degree varying from 5 to 20 % depending on the arc conditions. The plasma expands into the vessel which is kept at low pressure (typ. 0.25 mbar). Downstream monomers as SiH_4, C_2H_2 or CH_4 are injected. The formed plasma mixture flows towards a substrate holder where deposition takes place. A more extensive description of the set-up is given in [4,5,6,7].

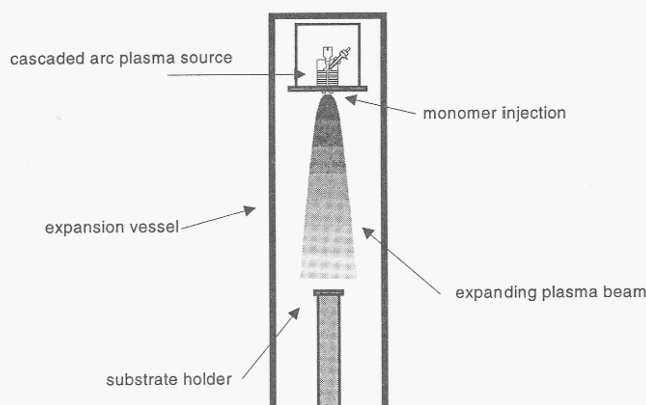

Figure 1. Schematic drawing of the expanding thermal arc plasma source.

An essential difference between the expanding thermal plasma deposition and the other high density plasma sources or the capacitively coupled discharges is the dissociation of the monomers injected. As the electron temperature is low in the expansion [8], the monomers can not be dissociated by means of electron impact. Instead they are dissociated by a chain of charge exchange with the Ar^+ ion produced in the arc, e.g. for acetylene

$$Ar^+ + C_2H_2 \rightarrow Ar + C_2H_2^+ \qquad (1)$$

followed by dissociative recombination of the formed molecular ion,

$$C_2H_2^+ + e \rightarrow \text{radicals} \qquad (2)$$

e.g. C_2H + H. The formed radicals are electronically and rovibrationally excited and, depending on the amount of ions left, undergo another sequence of charge exchange and dissociative recombination. The first step is the time limiting step with rates on the order of 10^{-15} - 10^{-17} m^3s^{-1} [9]. This manner of dissociation of the injected monomer is very efficient and the material freedom is large: all molecules having an ionization potential which is lower than that of argon can be dissociated by reactions analogous to Eqs. (1)-(2). Therefore similar arguments hold for the dissociation of SiH_4 and CH_4. Furthermore, by changing the monomer flow and the arc power or flow the dominant radical can be tuned. Note that the sequence of reaction Eqs. (1)-(2) leads to a decrease of the ionization degree of the plasma as observed by Langmuir probe measurements [6,10]. Therefore for the conditions mentioned the ion density close to the substrate will be on the order of the 10^{17}-10^{18} m^{-3} at electron temperatures in the range of 2000-3000 K. The self-bias is low typically 1.5 V. The substrate can be biased independently by applying an RF bias. Radical and ion fluxes are in the 10^{21}-10^{22} $m^{-2}s^{-1}$ and 10^{20}-10^{21} $m^{-2}s^{-1}$ range respectively.

Note that the chemical energy is contained in the ions and or radicals (for example atomic hydrogen which can be used to abstract e.g. SiH_4 to SiH_3) created in the cascaded arc plasma source and that the ions and or radicals emanating from the cascaded arc are used to dissociate and ionize the injected monomers. Note furthermore that due to the large pressure difference between arc and expansion vessel the source is truly geometrically separated. Another important difference is the larger level of flow and power. As also the efficiency is high a large flow of chemical active particles is obtained therewith bringing high deposition rates over large areas within reach.

a-C:H deposition

Using an Ar/C_2H_2 plasma a-C:H was deposited. Here we will discuss the results of arc current and C_2H_2 flow variation on the properties of the deposited a-C:H. During the deposition the argon flow was kept constant at 100 scc/s, and the pressure was 0.25 mbar. The temperature was not actively thermostrated but remained within the 20-90 °C range. The films which were deposited on glass substrates have similar properties, e.g. hydrogen content, sp^2/sp^3 ratio and bandgap, as a-C:H films produced using other techniques e.g. PECVD [11]. As is demonstrated by Gielen et al. [11] the refractive index in the infrared is a good parameter to classify the quality of the a-C:H deposited, i.e. a harder film has a higher refractive index. Therefore in this paper we will use the refractive index to

characterize the quality of the deposited a-C:H. In fig. 2a the refractive index n is shown as function of the C_2H_2 flow for three different arc currents. As can be seen the highest refractive index is obtained for the highest arc current and flow. As can be seen also for I_{arc}= 22 and 48 A the refractive index first increases and then decreases again. For I_{arc}=75 no maximum is observed. As we know from ionization degree measurements in a pure argon expanding plasma [8] the maximum in the refractive index is obtained approximately at a C_2H_2 flow value where the amount of ions equals the amount of C_2H_2 molecules injected. The decrease in refractive index can be explained by the fact that the extra C_2H_2 injected is not dissociated and deposits directly on the substrate. The direct C_2H_2 deposition is possible because it is known that C_2H_2 has a sticking probability equal to 1 for non passivated surfaces [12]. The growth rate obtained for the films deposited corresponding to fig. 2a is shown in fig. 2b. As a higher

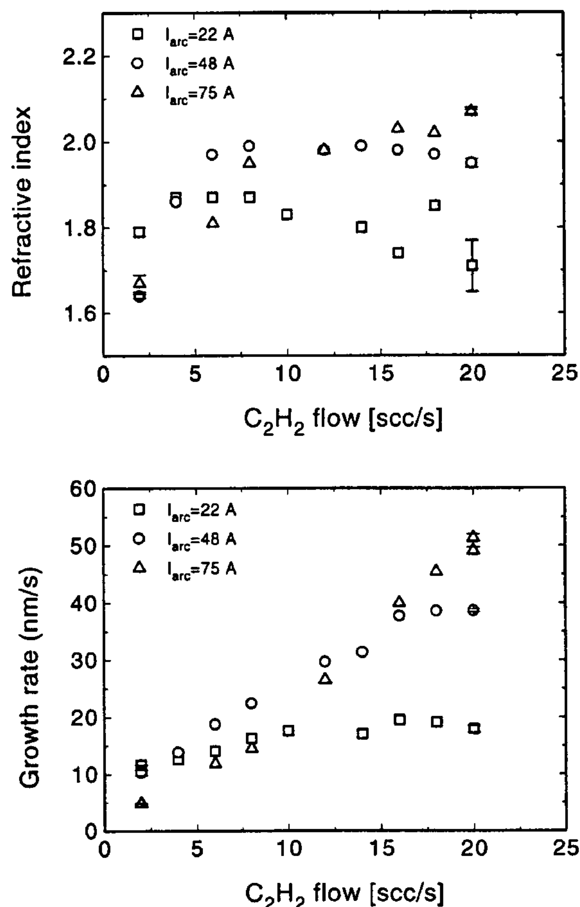

Figure 2. a) the refractive index (top) and b) the growth rate (bottom) vs. C_2H_2 flow for three different arc currents

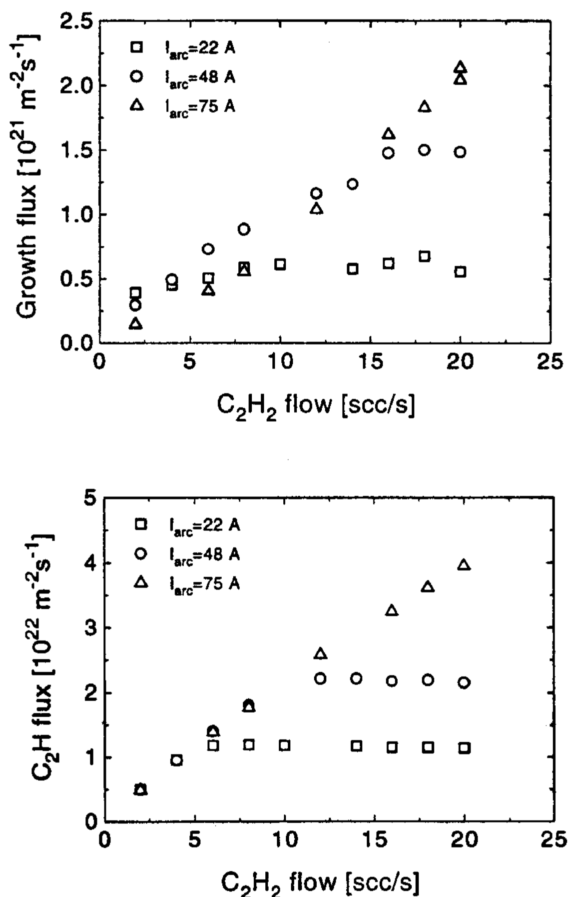

Figure 3. a) The C_2H flux as determined from the growth rate and density (top) and b) as determined using a simple plasma model (bottom).

refractive index means a harder film it can be concluded from fig. 2b that the quality increases with growth rate. The refractive index can be used to estimate the density ρ of the film by means of the relation $\rho = C(n^2 - 1)/(n^2 + 2)$ with C a constant which is equal to 1.6×10^{29} m^{-3}. By multiplying the growth rate R with the density ρ the effective growth flux Γ_{growth} is determined. As was mentioned the maximum refractive index as a function of C_2H_2 flow was observed at a flow at which the amount of argon ions approximately equals the amount of C_2H_2 molecules injected. As we know from other spectroscopic measurements the dominant reaction product of the dissociative recombination Eq. (2) is the formation of C_2H and H. Therefore if we assume that C_2H is the dominant precursor for growth we can use the growth flux to estimate the C_2H flux as is shown in fig. 3a. Using a simple model in which every Ar ion produced in the arc is converted into a C_2H radical which is not lost during the transport towards the substrate, the C_2H flux can be calculated from the injected C_2H_2 flow and the Ar^+ flux [11]. The result is shown in fig. 3b. Note the similarity of this figure with fig. 3a. Taking the ratio of the two fluxes the effective sticking probability of the C_2H can be determined. The result is shown in fig. 4. As

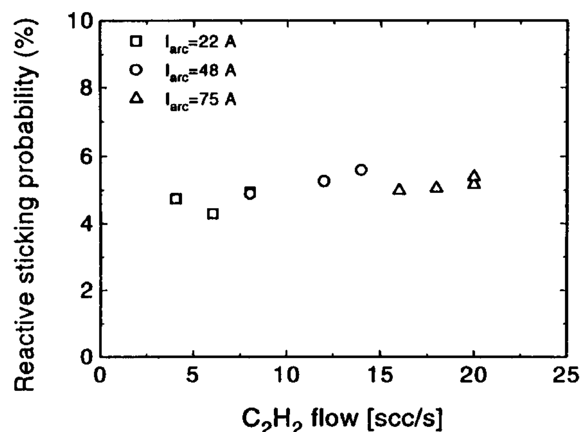

Figure 4. The effective sticking probability as determined from figs. 3a and 3b

can be seen the effective sticking probability is about 5%. In the calculation of the sticking probability we only took the data in a region around the maximum refractive index as we consider the assumptions made in the calculation to be only valid there. The 5% sticking probability should be compared with the sticking probability usually assumed for C_2H which is 1. Therefore we think that the chemisorption of C_2H on a growing a-C:H surface is strongly dependent on the hydrogen passivation of the surface [12] and thus the effective sticking probability of the C_2H radical in presence of large H radical fluxes is determined. This large H flux probably leads to a passivated surface on which the sticking of the C_2H radical only occurs on a dangling bond similar to the sticking of C_2H_2 on silicon surfaces [12]. With other words the 5% probably indicates that the surface is highly passivated. Note the absence of ion induced deposition, as the self bias is in the 1.5 eV range. For these ion energies in this range the deposition mechanism must be considered purely surface determined as the penetration depth is less than one monolayer [13]. The independence of the deposition on the substrate temperature makes a direct chemisorbed incorporation of the C_2H radical the most logical.

Conclusions

To conclude we have demonstrated that good quality a-C:H can be deposited at large growth rates. Moreover we have demonstrated that the larger the growth rate the larger the refractive index. The effective sticking probability of the C_2H radical in presence of large H radical fluxes is determined and is found to be 5%. Of this value depends strongly on the assumptions made and further research is necessary to substantiate the results obtained.

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