Pure & Appl. Chem., Vol. 64, No. 5, pp. 731–737, 1992.
Printed in Great Britain.
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Process and property relationships in hard coatings made by plasma and ion-assisted methods

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Abstract - This paper discusses the basic phenomena and process-property relations in the deposition of hard coatings. Two approaches are considered: the plasma assisted chemical vapor deposition and ion assisted physical vapor deposition methods (PA-CVD and IA-PVD respectively). In PA-CVD the plasma is used to activate the gaseous precursors and the film is formed during ion-molecule and radical-molecule reactions in the plasma bulk and at the plasma-surface boundary. In IA-PVD partially ionized metal vapor is admitted into an argon supported plasma together with a reactive gas. These are the film precursors which react at the substrate surface under intense ion bombardment and at reduced pressure. The correlation between experimental variables and properties of the deposits is illustrated with hard nitride films namely silicon nitride Si_3N_4 made by PA-CVD and titanium nitride TiN made by IA-PVD. Two picostructural examples are illustrated: argon entrapment in TiN made by IA-PVD, and lattice strain effects on the Raman spectrum of diamond films made by (microwave) PA-CVD.

INTRODUCTION

Plasma and ion-assisted processes play an important role in vapor deposition procedures. They permit the coating and surface modification of heat-sensitive materials. In addition, they allow such treatment steps as the preheating, cleaning and etching, and hardening of substrates to be executed in a single batch sequence. Combined with other advantages such as a reasonably high deposition rate, good adhesion and a wide spectrum of processes, this explains the growing interest in plasma and ion-assisted methods.

The present paper discusses the effect of deposition conditions on the composition and structure of films made following two of the most widely used techniques: plasma assisted chemical vapor deposition (PA-CVD) and ion assisted physical vapor deposition (IA-PVD). In PA-CVD the film is formed in a sequence of ion-molecule and radical-molecule reactions in the plasma bulk and at the plasma-surface boundary. Consequently the deposition rate and the properties of the resultant film are strongly affected by the ion-to-radical density ratio in the plasma and by the balance between plasma-bulk and plasma-surface processes. In IA-PVD metallic vapor and plasma activated gaseous reactants coalesce on a negatively biased surface and the film is exposed during deposition to an intense ion bombardment which strongly influences its structure. The correlation between experimental variables and the properties of films made by the techniques are illustrated by typical products, namely silicon nitride Si_3N_4 made by PA-CVD and titanium nitride TiN made by IA-PVD.

The microstructure of films deposited from plasma activated processes is well described in terms of the Movchan-Demchishin-Thornton models (ref. 1). These describe collectively how the grain morphology and topography are controlled by a set of superposed parameters which include the substrate temperature, inert gas partial pressure and substrate bias. The detailed microstructure is also affected by the substrate itself (refs. 2-4) which influences the nucleation and thus the grain size of the growing film, and also by the rate of deposition through shadowing effects (ref. 5).

On a much finer scale the structure within the individual grains themselves, i.e. at an atomic order level and which is generally termed the picostructure (ref. 6), is affected by the deposition conditions, such as the ion-to-neutral ratio (ref. 7) and the deposition geometry (ref. 8). Thus, in process parameter terms, the picostructure is affected by the applied substrate bias and the ion and neutral current density flowing to the substrate during the deposition process. A particular interest in the studies of the picostructure is the type and quantity of defects such as vacant lattice sites, dislocation loops and residual strain effects associated with the local lattice distortion. These all affect the physical (electronic) as well as the mechanical properties of the films, as does the microstructure itself.

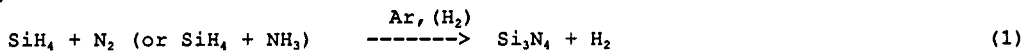
PLASMA-ASSISTED CHEMICAL VAPOR DEPOSITION

Plasma assisted chemical vapor deposition is carried out in a vacuum tight reactor chamber in which an electromagnetic field is applied across the feed gas supply, the plasma is ignited and the deposition process takes place (ref. 9). A non-equilibrium nature together with a high energy content are the major features of a weakly ionized low pressure plasma. Each of the plasma constituents has its own characteristic energy distribution; a Boltzmann distribution of the bound levels and the Saha-Eggert equation for the density of the charged particles do not hold. The kinetic energy of the ions may be 2 to 3 times that of the neutral species (<0.3eV as opposed to about 0.05eV) but still negligible when compared with that of free electrons (which is normally in the range 1 - 10eV) (refs. 10,11).

The reaction sequence leading to the deposition of a film starts with electron-neutral collisions, termed the primary reactions, in which excited monomers, radicals and ion-radical intermediates are formed; the production of ions, atoms and radicals has been discussed in a number of reviews (refs. 12-18). The process continues through secondary ion-molecule and radical-molecule reactions between the products of the primary reactions with fresh gas to form the required deposit (refs. 18,19); ion and radical reactions have also been reviewed (refs. 16,17,20-22). The mathematical product of ion (or radical) density in the plasma with the cross-section for the corresponding ion-molecule (or radical-molecule) reaction was suggested (refs. 23,24) as a "probability criterion" to define the rate determining mechanism. The effect of the balance between plasma-bulk and plasma-surface processes is illustrated below by the low pressure deposition of diamond. The deposition of silicon nitride Si_3N_4 is a typical example of the effect of ion-to-radical ratio.

FEATURES OF PA-CVD SILICON NITRIDE

Silicon nitride is formed by reacting a silicon-containing source gas such as silane SiH_4 or silicon tetrachloride $SiCl_4$ with a nitriding agent such as ammonia or nitrogen (refs. 9,25,26):



$$SiH_4 + N_2 \text{ (or } SiH_4 + NH_3) \xrightarrow{Ar, (H_2)} Si_3N_4 + H_2 \quad (1)$$

$$SiCl_4 + N_2 \text{ (or } SiCl_4 + NH_3) \xrightarrow{Ar, (H_2)} Si_3N_4 + HCl \quad (2)$$

In an RF induced electrodeless system (ref. 26) the deposition rate and the residual chlorine concentration in the film depend on the RF input power, on the bias applied to the substrate, and on the position of the substrate with respect to the direction of the gas flow and the induction coil. It was found (ref. 26) that the deposition rate at 100 W (at a constant gas pressure of 5 Torr) on an electrically floating substrate is higher than that on a grounded substrate by a factor of two. An increase in the input power causes a reversal in this trend and at 200 W the deposition rate on the grounded surface exceeds that on the floating one.

The amount of trapped chlorine increases with increasing RF power on a grounded substrate, but remains almost constant on a floating substrate. As a result, the content on a grounded film made at 200 W is five times higher than on a film formed on an electrically floating substrate. Chlorine-rich positively charged species, formed in the gas phase, constitute the major source of trapped chlorine. Other sources of chlorine contamination arise from an insufficient dissociation of the starting $SiCl_4$ monomer, and, when hydrogen and ammonia are present in the feed gas, HCl and chlorine from the gas phase. If the substrate is mounted downstream beyond the RF coil, it traps increasing amounts of reaction by-products. An increased degree of dissociation of the HCl along the reaction tube leads to a corresponding increase of chlorine both in the gas phase and in the film (refs. 24,27,28).

The concentration of trapped chlorine is defined by the radical-to-ion ratio in the plasma and can be reduced by adding hydrogen or a superstoichiometric concentration of ammonia. The hydrogen/ammonia combination, the input power, and the bias applied to the substrate are the variables which determine the radical-to-ion ratio in the plasma and hence the deposition rate and amount of trapped chlorine in the film. Electron spin resonance studies (refs. 23,24) of plasma-born species collected on pre-treated alumina show that the main effect of the addition of hydrogen or ammonia is to increase the free radical concentration in the plasma. Added hydrogen also markedly inhibits both the mean electron energy and also the positive ion energy in the plasma (refs. 23,24). Mass spectrometry indicates in addition that the presence in the feed gas of excessive amounts of hydrogen or ammonia cause a decrease in the concentration of chlorine-rich Si_xCl_y polymerized species (ref. 23). At high input power this trend is reversed (ref. 23): an increase in the ion density and an enhanced formation of chlorine-rich positively charged species. These latter are accelerated towards the negatively biased substrate, increasing both the deposition rate and the chlorine concentration in the film. In contrast, at low input power, large concentrations of free radicals in a hydrogen or ammonia rich plasma promote the radical-molecule mechanisms and inhibit the formation of the chlorine-rich Si_xCl_y positively charged species. A low concentration of such ions leads to a low chlorine concentration in films at floating potential (ref. 26) whereas the high concentration of the radical preserves the high deposition rate.

The results can be summarized as follows. If the conditions for plasma activated deposition are defined for a situation where an equal competition between ion and radical precursors exist, then a reliable control of their balance and of the surface potential is a requirement for the consistent reproducibility of the characteristics of a given film.

ION-ASSISTED PHYSICAL VAPOR DEPOSITION

Among the methods currently used to deposit films by physical vapor deposition, three methods: magnetron sputtering, low voltage high current electron beam evaporation, and cathodic arc evaporation hold a particular interest in the present discussion, because all are used extensively at an industrial level. The main difference between the methods is the degree of ionization of the metal vapor which increases in the given order (refs. 29,30). All three methods allow the metal vapor to be introduced into an argon-supported plasma together with a reactive gas such as nitrogen. The substrate materials to be coated are included within the plasma and are biased with a negative potential. The result is a technology termed ion assisted physical vapor deposition which is used extensively to make films of compounds such as the nitrides of the group IV B metals titanium, zirconium and hafnium. These are used in wear and abrasion resistant applications as well as in purely decorative functions.

The deposition of the metal ions and neutrals from the source is "line of sight" in every case. The substrates are rotated, often in a planetary motion, to ensure uniformity of coating properties such as the thickness and color. In the present study this is significant because the data measured on the individual samples are thus typical of the conditions existing within the deposition unit as a whole.

It is thought that the reaction of the depositing species occurs at the substrate surface. The arriving species are ions of metal vapor, reactive gas and argon, as well as the so-called fast neutrals. These can be atoms of any of the species which have either gained energy from collisions with charged particles or have retained their energy but lost their charge through charge transfer. In the specific case of cathodic arc evaporation, there is also a species which is the micron size particles, termed macros, emitted from the arc source in quantities which depend on the evaporation current and voltage.

PICOSTRUCTURAL FEATURES OF IA-PVD NITRIDES

There is a limited number of techniques available to study the structure of films at an atomic level. Transmission electron microscopy (TEM) gives information on the presence of defects such as dislocation networks and loops. Positron annihilation spectroscopy (PAS) allows the presence of vacant lattice sites and other open volume defects to be detected. X-ray diffraction (XRD with a Bragg-Brentano goniometer) allows the lattice plane spacings parallel to the surface to be determined, the presence of residual stresses to be studied and strain distributions to be made evident. Results from studies of titanium nitride TiN films made by IA-PVD methods are now reviewed.

Transmission electron microscopy

The effect of the deposition conditions on the defect structure has been demonstrated in a number of key pieces of work. A study (ref. 31) of the effect of the bias voltage on reactively sputtered TiN films showed a massive increase in the dislocation density on changing the bias from -80V to -120V. Indeed the dislocation density at -80V and less negative was quite low with individual dislocations being clearly resolvable. At bias values of -120V and greater, there were so many dislocations that their individual nature or their presence as fine intrinsic or extrinsic loops could not be resolved. The study (ref. 31) also showed that a bias of greater than -40 V is required to avoid the presence of intergranular voids. Further work (ref. 7) has shown that an increase in the ion-to-atom ratio also increases the amount of damage which is caused in the film deposited, as indicated in the Introduction. When individual dislocation loops are resolvable, they are found (ref. 32) to be extrinsic in nature and habit the (111) family of planes.

If the deposition is made at very high bias levels, ultramicrocracking can be observed (refs. 33,34) on specific lattice planes within the individual grains themselves. In the case of TiN the cracking is on the (220) family of planes which is the slip plane of this material (ref. 32).

X-ray diffraction studies

The standard method of XRD study, the Bragg Brentano goniometer, returns lattice parameters measured on planes lying parallel to the surface of the sample. Hence the grains studied are uniquely defined by their crystal orientation. If the stress in the sample is simple biaxial, then the lattice parameters derived from the individual peaks are the same, taking the effects of the x-ray elastic constants into account (TiN is very nearly elastically isotropic (ref. 35)). A series of samples made at increasing bias values are shown in Fig. 1a, where the initial smooth increase reflects a build up of biaxial residual stress in the plane of the sample (compression in the plane causes a

Poisson's ratio expansion in the perpendicular direction, which the XRD records). In this series of samples there is a change in behavior at biases of -90 V and more negative, where the behavior of the different grains changes dramatically. It is assumed, but not yet proven, that this change is related to the massive increase in the density of dislocations and loop type defects discussed above.

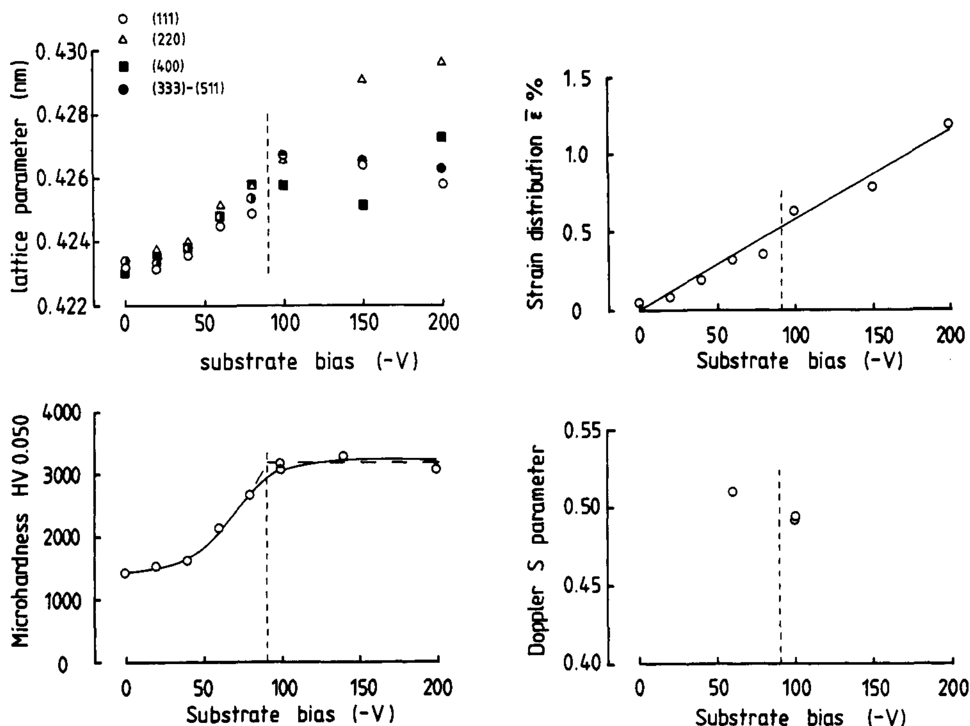


Fig. 1. Picostructural data on TiN made by IA-PVD as a function of substrate bias at a target power of 10 kW, a) lattice parameters taken from the XRD peaks indicated, b) lattice strain distribution, c) microhardness, and d) Doppler PAS (S-parameter) results.

The widths of the XRD diffraction peaks (with instrumental broadening subtracted) allows the distribution of the strains in the lattice to be derived from the Williamson-Hall plot (ref. 36). The results for the samples whose lattice parameters are shown in Fig. 1a, are given in Fig. 1b, where it is apparent that the lattice distortion continues to increase with bias.

It is to be expected that these defects should affect the mechanical properties of the films. At the present time, only data for microhardness have been recorded. These are shown in Fig. 1c. An open question is whether the hardness in these films can be used as a guide to the wear resistance. If the above discussion is correct, that the defective nature of the lattice is increasing, then it might be anticipated that the wear properties might be adversely affected at very negative bias levels.

Positron annihilation spectroscopy

There are two ways in which the annihilation of fast positrons can be viewed to give information on the presence of vacancies and other open lattice defects. The first is Doppler measurement where the peak width at half maximum (termed the S-parameter) is taken as a measure of the total defect fraction in the sample. In the second the lifetimes of the positrons are determined and the spectrum is usually analyzed into three components. The shortest lifetime is that in the free lattice, whilst the longer ones are related to the defects present, the greater the lifetime the larger the volume of the defect (i.e., the lower the probability of the positron finding an electron).

S-parameter results for samples above and below the transition at -90V, as given by the XRD data, are included in Fig. 1d as taken from a study which is currently in hand. It is apparent that there is a much greater fraction of open volume defects present at the lower bias. The lifetime data (not shown) indicate that there is a smaller number of larger defects at low bias values, and a larger number of smaller defects at the more negative bias values. Taken together, the data indicate a greater tendency for the growing film to retain vacancies when grown at lower bias values. At higher bias values, it appears that the generation of large dislocation densities allows any vacancies retained during deposition to reach the vacancy sinks which dislocations offer.

Argon entrapment in IA-PVD films

The difficulties of interpreting studies of the picostructure of films made by IA-PVD can be illustrated by the question of argon entrapment in growing films, which is not yet resolved.

As argon is used to support the plasma when making films using IA-PVD processes, it might reasonably be expected that some argon remains trapped in the growing film, and this indeed happens. Of the techniques discussed above, only TEM and XRD can be used to give more detailed information as PAS is only applicable to open volume defects.

There are two sets of XRD results (refs. 37,38) which show an apparent correlation between the amount of trapped argon and the lattice parameters of, specifically, the (111) family of planes in TiN. One set of data (ref. 37), shown in Fig. 2a, is taken from a set of samples deposited at different rates, but otherwise identical conditions. The other shown in Fig. 2b is made at increasing bias values (ref. 38). It is tempting to assume that this correlation is not fortuitous, e.g. the argon may be retained in the extrinsic loops (ref. 32) which are formed on (111) planes. These are believed (ref. 6) to modify the intrinsic stress resulting from the deposition process by causing a lattice expansion parallel to the growth direction (and hence a contraction in the plane of the film). An alternative possibility is that the residual stress results directly from the presence of argon, but measurements show (refs. 39,40) that the residual compressive stress is not proportional to the argon content.

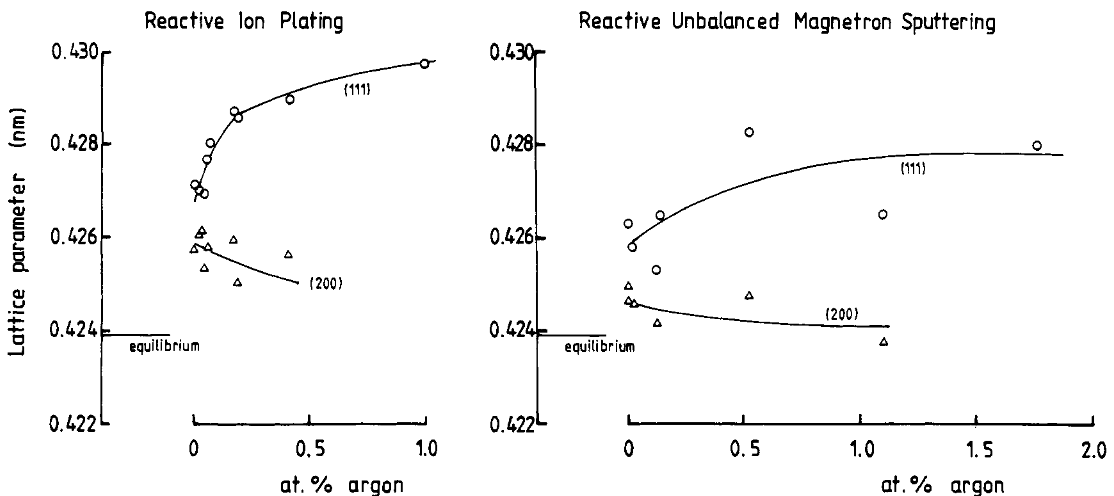


Fig. 2. The effect of entrapped argon on the lattice parameters of TiN films made by IA-PVD methods, a) reactive ion plating (ref. 37), and b) unbalanced magnetron sputtering (ref. 38).

In contrast to the XRD data, TEM studies (ref. 4) do not support the existence of a correlation between argon entrapment and a (111) texture. The argon content in epitaxially grown TiN films decreased in the sequence (110), (100) and (111).

At the present time, it is not clear how the behavior is to be explained. As illustrated above, it is likely that the conditions under which the films were made has an effect: both sets of XRD data were made on films deposited at high rates where the lattice is highly defective. In contrast, the TEM work was carried out on samples deposited at the very low rates needed to make single crystals. Further work is needed to clarify this situation.

PICOSTRUCTURAL STUDY OF DIAMOND FILMS

Diamond films can be deposited using PA-CVD methods whereby a hydrocarbon-hydrogen or a hydrocarbon-hydrogen-oxygen plasma is formed with a large excess of hydrogen atoms present. Diamond is formed as a metastable material in continuous competition with other carbon phases. Starting with plasma bulk reactions and continuing through heterogeneous processes at the plasma-surface boundary, this competition can be thought to conclude only after the diamond sp^3 structure is stabilized.

Three major steps can be discerned in diamond formation (ref. 42): first, dissociation of the hydrocarbon source gas and the formation of intermediate species, second, transport to the substrate surface, and third, the stabilization of the diamond structure. The nature of the starting monomer has very little effect on the resulting film (refs. 43,44) suggesting that, regardless of the starting material, intermediate species containing similar groups of one or two carbon atoms are the building blocks for the diamond film. The precise mechanism for diamond formation is still being studied, but

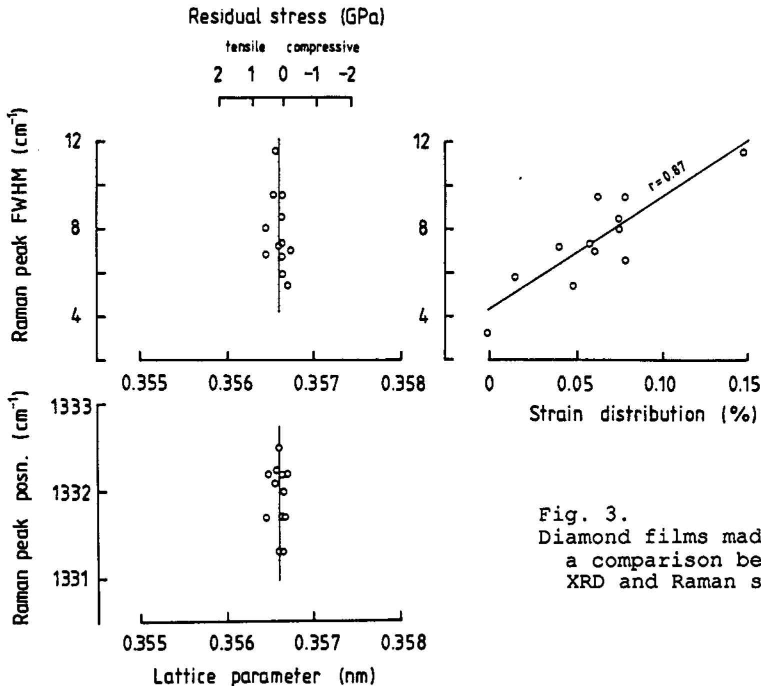


Fig. 3.
Diamond films made by (microwave) PA-CVD: a comparison between data measured by XRD and Raman spectroscopy.

it is clear that once the diamond film has been nucleated the formation of graphite and/or other non-diamond phases must be inhibited. This is achieved by controlling the surface processes and substrate bias. In addition to inhibiting polymerization processes in the gas phase, the high concentration of hydrogen contributes to the purity of the film by passifying the dangling bonds of the surface carbon atoms and by selectively etching the graphitic phase. In addition, the surface bias is regulated to reduce ion bombardment of the growing diamond film which may otherwise induce long range structural changes and, by local heating, its graphitization (ref. 42).

As is apparent from the earlier discussions, there are few methods available that give information on the picostructure. In diamond films, XRD is only used to a limited extent because of its very great penetrating power which records the substrate spectrum causing overlap and interpretational difficulties. As an alternative, Raman spectroscopy returns a peak at 1332 cm^{-1} (which is the principle way of identifying that a material is diamond) the position and full width at half maximum (FWHM) of which are believed to be affected by stress and strain distribution effects, analogous to the situation seen by XRD.

As a test of the validity of using this method for measuring strain distribution, diamond films deposited by microwave PA-CVD onto cemented carbide have been studied both by XRD and Raman spectroscopy. The deposition conditions were chosen to give a poor adhesion and thus a low residual stress in the films. The results are shown in Fig. 3, where the XRD data are taken as abscissae and the Raman peak position and width as ordinates. The lattice parameters allow the residual stress in the film to be calculated from the elastic constants; this scale is given as the upper abscissa. The data show that the strain distribution measured by both methods can be correlated directly with a coefficient of regression r of 0.87. In contrast, although there is a variation in the position of the Raman peak, it is not apparently affected by the small levels of stress present in the films. Clearly some other, as yet undefined, factor is affecting the location of the Raman peak.

CONCLUSIONS

- The plasma activation of a deposition process affects very much the possibility of a chemical reaction happening and influences additionally the microstructure of the films.
- In PA-CVD reactions where equal competition between ion and radical precursors exists, their balance must be controlled very carefully to allow reproducibility of film properties.
- Films deposited by IA-PVD methods can be damaged at a picostructural level to an extent which depends on the deposition conditions. The damage affects the physical properties of the films and it is assumed that the mechanical properties are also affected; this is still being studied.
- in diamond films made by (microwave) PA-CVD, the strain distribution can be measured equally well from XRD Williamson-Hall plots and Raman peak width analysis. The position of the Raman peak is not only affected by residual stress but also by other, as yet unidentified, factors.

Acknowledgements
The authors wish to thank Mr. William Drawl and Ms. Diane Knight of the Pennsylvania State University for making the diamond films and carrying out the Raman spectroscopy respectively. They are also grateful to Dr. W.-Dieter Munz, Professor R. Avni and Professor Vaclav Valvoda for many useful discussions.

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