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Modeling of ta-C growth: Influence of the technological parameters

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ABSTRACT

The structure of tetrahedral bonded amorphous carbon (ta-C) is determined by the energy of the impinging carbon ions, the angle of incidence, the substrate temperature and the deposition rate. Up to now modeling of the ta-C growth was concentrated on the energy effects by investigating the early stages of the ion impact and the short-time relaxation in the thermal spike. A new analytical model is presented, which emphasizes the role of long-time diffusion, driven by the stress induced drift towards the surface. In accordance with the experimentally found trends, the model allows the estimation of the sp^3 content in dependence on the technological relevant deposition parameters ion energy, angle, temperature, rate and their distributions. This opens the way for the realistic simulation of ta-C growth in industrial coaters.

1. Introduction

Tetrahedral bonded amorphous carbon (ta-C) represents a very promising kind of carbon modifications. The short-range surrounding of most of the carbon atoms corresponds to the (although some distorted) four-fold coordination of diamond (sp^3 bonds), the high-pressure modification of carbon. Hence, its mechanical properties approach for the highest sp^3 contents those of diamond (Young's modulus up to 850 GPa and hardness up to 80 GPa in comparison to 1163 GPa and about 100 GPa for polycrystalline diamond, respectively). The preparation of diamond films demands high-temperature CVD with high substrate temperatures, preferably around 900 °C. In contrary the ta-C deposition occurs at low temperatures, if possible below 100 °C. The key factor is the sufficient high kinetic energy of the impinging carbon particles. According to the subplantation growth concept, introduced by Lifshitz and co-workers [1,2] the carbon ions penetrate into the uppermost surface layers. This growth mode is a unique peculiarity of carbon due to its combination of high bonding strength and low atomic mass, which results in low sputter yield and rather deep penetration. For other materials sputtering would exceed deposition in the energy range, necessary for sufficient penetration. Below the surface the incorporated carbon atom is compressed by its surrounding. Hence, the formation of sp^3 bonds as in diamond is favored. Low deposition temperatures are necessary to avoid a relaxation of this non-equilibrium structure by a $sp^3 \rightarrow sp^2$ transition to a more graphitic bonding state.

The numerous experimental investigations of the sp^3 fraction s in dependence on the particle energy ε and on the substrate temperature T gave concordantly the following general rules:

- For room temperature deposition, the sp^3 content increases above a certain threshold of about 20 eV up to a maximum at around 100 eV.
- At given particle energy, the sp^3 content decreases with rising substrate temperature.

However, there are some remarkable differences, which could be attributed to differences in the deposition conditions [3–9]: for mass selected ion beam deposition (MSIBD) with monoenergetic ions and very low rate, the descent $s(\varepsilon, T=\text{const.})$ beyond the maximum is rather slight, but the slope $s(\varepsilon=\text{const.}, T)$ with rising temperature is rather steep [6,10–13]. In contrary for pulsed laser deposition (PLD) or vacuum arc with broad energy distributions and higher rates, there is a much stronger decline after the energy maximum and a more gradual temperature dependence. Additional factors influencing the sp^3 content are the linear deposition rate $w = dh/dt$ (h = film thickness) and the angle of incidence ϑ, measured against the surface normal. An inclined deposition leads above a critical angle ϑ_c to a rather steep drop of the sp^3 fraction [14,15].

The safe control of these various factors is especially important in the light of the increasing industrial application of ta-C films, which demands a reliable assessment of the coatings to be expected even in the realistic case of complex sources and complex geometries. Modeling may be a suitable tool, to restrict or even to avoid extensive test series, otherwise necessary for optimization.

2. Modeling of ta-C growth

The formation of ta-C films is a very complex phenomenon, including a lot of different processes. They occur over a very broad

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time scale from 10^{-14} s up to some seconds. For a better overview, the growth process may be separated into four subsequent stages with different external conditions and different internal mechanisms: the collisional stage ($\leq 10^{-13}$ s), the thermalization stage($\approx 10^{-13}$–10^{-11} s), the diffusional stage ($\approx 10^{-11}$–1 s) and the technological stage (≥ 1 s). In the collisional stage the incoming carbon ions are stopped by collisions with the atoms in the surface region, losing its energy by ionization, electronic excitation and especially by displacing the atoms within a collision cascade including phonon excitation. In the thermalization stage this excess energy initially localized within the cascade will be rapidly distributed over its surrounding. In the diffusional stage the final bonding structure develops in the competition between the local sp^3 stabilization and the sp^2 relaxation by diffusion towards the surface. In the technological stage the varying conditions in industrial coaters due to the rotation of the substrates and an aimed layered design must be considered.

Up to now the simulations of the complex ta-C growth are concentrated on the early process stages, the collisional and the thermalization stage, with the main objective to describe the non-monotonic energy dependence of the sp^3 content or of related parameters. Details of the collisional and the thermalization stage have been investigated by molecular dynamic simulations [16–21]. To limit the computational efforts to an acceptable level, most investigations use empirical potentials, fitted to experimental results. (The optimization of the potentials by comparing MD results with the final ta-C structure is problematic, because the output of the thermalization stage is overlayed by the subsequent diffusion processes.) But even with this approximation, only newer investigations are able to handle sufficient ion impacts to achieve a stationary film growth for thicknesses of some nanometers [16,17,20].

The analytical approaches of Robertson [21,22], Davis [23], the Hofsäss group [7] and of Kalinichenko et al. [24] use for the collisional stage the results of Monte-Carlo calculations within the TRIM program. The widely used SRIM program package (= Stopping and Range of Ions in Matter) with its core TRIM program (TRansport of Ions in Matter, www.srim.org) assumes binary collisions within an amorphous target, where the impact parameters of the subsequent collisions are randomly selected [25,26]. The subsequent thermalization is treated by the thermal spike model, where the local excitation of the atomic lattice is described within the framework of a continuum model by the transient temperature field in the surrounding of a point source [21–23] or a line source [7,24]. According to the early concepts of Robertson and Davis, the structures with high sp^3 content (reflected by increased density or high compressive stress) are created during the collisional stage and then partially transformed to sp^2 bonds by structural relaxation in the thermal spike. Both effects, sp^3 formation and sp^3 relaxation, are favored by higher ion energies, but to a different degree: At lower energies the formation is dominating, at high energies the relaxation, thus resulting in an energy optimum for maximal sp^3 bonds. In the newer approaches of Hofsäss [7] and of Kalinichenko [24] the collision cascade determines only the initial energy concentration, whereas their transformation into the ta-C structure occurs inside the thermal spike. According to the Hofsäss model the sp^3 bonds are formed by the intense thermally activated atomic restructurization within the excited thermal spike region. The intensity of this structural modification is characterized by the mean number of rearrangements per atom within the hot zone, i.e. by the ratio N_T/N_S of rearrangements N_T to atoms N_S in the thermal spike region. Due to the short available time the main contribution comes from atoms with thermal energies above the activation energy for local rearrangement $q' \approx 3$ eV. For not too high energies below about 100 eV, N_T/N_S increases with the energy ε of the impinging ions. But for higher ion energies this trend is reversed: 1) an increasing part of the ion energy is transferred to electronic excitations, which in the short available time are not converted into thermal energy, 2) due to the increasing number of recoiled target atoms, the energy is spread over a larger cascade volume leading to a reduced energy concentration and corresponding to less redistribution. In [24] the additional effect of high pressure $p(t, \varepsilon)$ in the overheated nano-region is considered by replacing q' by $q' - p(t, \varepsilon) \cdot \Delta v$, where Δv represents the reduction of the atomic volume in the transition from sp^2 bonding to sp^3 states. Again the non-monotonic energy dependence of the rearrangements in the thermoelastic peak reflects the corresponding course of the initial energy distribution (or initial temperature) due to the increasing excitation volume in combination with the reduced fraction of thermal energy.

The energy concentration will rapidly decay from very high values above some electron volt per atom to below 1 meV within about 10^{-11} s corresponding to temperature enhancements above 10,000 K and below some K, respectively [27,28]. Undoubtedly, the very excited initial stages will be of very importance for the formation of a first metastable atomic arrangement. However, it is questionable, how even rather small changes of the substrate temperature could markedly influence this high temperature short time relaxation and longer times must be considered [29]. Also the influences of inclined impingement and of the sp^3 favoring effect of higher deposition rates are outside the scope of these models. But from the technological point of view, just these factors apart from not too high ion energies are of special interest.

In the following, a complementary model is presented, which emphasizes the role of long-time relaxation. It will be presumed, that after some short-time relaxation (below the picosecond range) an initial ta-C structure has been established with a certain sp^3 fraction s_0. This metastable starting structure will in a long-time process relax towards the final stable structure, which is experimentally accessible. The resulting sp^3 fraction is determined by the competition of sp^3 conservation due to local rearrangement and the sp^3–sp^2 transition by drift towards the stress-free surface. In a semi-quantitative approach it will then be possible to describe the influence of the main technological parameters, the mean and the spread of the particle energy, the angle of incidence, the substrate temperature and the deposition rate on the sp^3 content in the amorphous carbon film.

3. Surface induced relaxation

The energetic carbon ions penetrate the surface and will be stopped as a neutralized atom after a certain distance l. This penetration length is (within a certain scatter) determined by the entrance energy ε: $l(\varepsilon)$. For oblique incidence under an angle ϑ against the surface normal, the final position is in a depth $d(\varepsilon, \vartheta) = l(\varepsilon) \cdot \cos\vartheta$ from the surface. Fig. 1 shows $l(\varepsilon)$ according to the Monte-Carlo code TRIM within the program package SRIM-2008 [30]. SRIM has been mainly developed

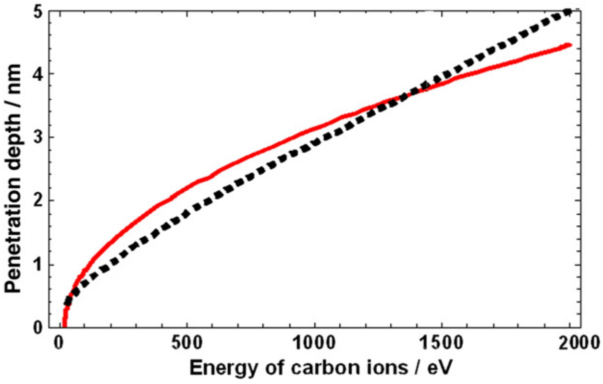

Fig. 1. Dependence of penetration depth on the energy of the impinging particles: continuous: approximation according to Eq. (1), dashed: according to TRIM code (C ions into carbon substrate with density 3.0 g/cm³).