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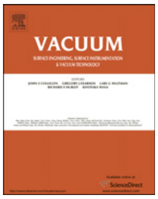

A comparative analysis of *a*-C:H films deposited from five hydrocarbons by thermal desorption spectroscopy

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ABSTRACT

Thermal induced gas evolution studies were performed on hydrogenated amorphous carbon (*a*-C:H) films deposited by plasma enhanced chemical vapour deposition (PECVD). The hydrocarbon–argon discharges were powered by asymmetric bipolar voltage pulses. Five different hydrocarbons (acetylene C_2H_2, isobutene C_4H_8, cyclopentene C_5H_8, toluene C_7H_8 and cycloheptatriene C_7H_8) were compared as film growth precursors.

The films were heated in vacuum upto 1000 °C and at the same time the gaseous effusion products were measured with a quadrupole mass spectrometer (QMS). The release of hydrogen, water, argon and different hydrocarbons from CH_4 upto C_7H_8 was proved. Large hydrocarbons were detected only when heating up soft films. When annealing hard films, they almost only lost hydrogen – mainly as H_2 but also in remarkable portion as H_2O. Possibly, the water in the *a*-C:H films contains the main fraction of hydrogen unbounded to carbon.

The characteristic temperatures for the onset of gas evolution of the molecular gases and of argon were found to be strictly correlated with the film hardness – independent of the film growth precursor. The threshold temperature for the release of the dominating effusion product, molecular hydrogen, is significantly higher than that of argon only for films with hardness below about 13 GPa.

1. Introduction

In hydrogenated amorphous carbon (*a*-C:H) films the carbon atoms occupy two substantially different bonding configurations: those associated with threefold plane coordination and sp^2 hybridization of the valence orbital and those with fourfold tetrahedral coordination and sp^3 hybridization. Depending on the hydrogen content and the carbon bonding state in these films different *a*-C:H phases exist [1,2]. For *a*-C:H deposited by PECVD at relatively low temperature two phases are relevant: under conditions of low ion bombardment a soft, polymer-like material is deposited with a high hydrogen content and predominantly sp^3 bonded carbon; with proper ion bombardment a hard hydrogenated carbon material is formed with predominantly sp^2 bonded carbon and a lower hydrogen content of about 20–35 at.%. For historical reasons the latter has been named diamond-like carbon, DLC. The optimum ion energy flux for the PECVD of DLC is in the order of 50–100 eV per deposited carbon atom [3]. Above all at higher deposition temperatures a graphite-like *a*-C:H forms, characterized by a low H content (less than 20%), a high sp^2 content and sp^2 clustering.

The mechanical properties of *a*-C:H depend on three correlating characteristics: (a) the carbon bonding structure, (b) the hydrogen content as well as (c) the size distribution and volume fraction of voids in the film. The void formation is associated with the presence of bond terminators like H and CH_3 groups in the films [4]. The volume fraction of voids was described by a filling factor, defined as the ratio of the total film volume to the volume occupied by carbon and hydrogen atoms [5].

Thermal desorption spectroscopy (TDS) [6] is an established method and was also applied to gain information about the thermal stability, the chemical bonds as well as the microstructure of thin films. Relevant results about *a*-C:H films will be presented in later paragraphs. The thermally induced changes in *a*-C:H film structure were also traced with complementary methods. In a study by Wu et al. [7] about 300 nm thick DLC films, deposited by an ion beam deposition technique from methane, were analysed after rapid thermal annealing (RTA) for 2 min at several fixed temperatures in nitrogen atmosphere. The hydrogen content of the films remained constant at 30 at.% upto 500 °C, decreased rapidly from 25% to 9% in the range 600–800 °C and finally remained at 5% in the range 900–1000 °C. The Raman spectra of these films did not change in

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the RTA temperature range from 25 °C to 400 °C and began to show the appearance of crystalline graphitic carbon above 500 °C.

Films with initially 40 at.% hydrogen were found to be structurally stable upto 260 °C [8]. A significant conversion to nanocrystalline graphite was detected by Raman spectroscopy already at temperatures above 300 °C and it was completed upon heating to 450–600 °C. A neutron diffraction study on the structure of hard *a*-C:H upto 1000 °C [9] showed the effect of elevated temperatures on the atomic correlations. The room temperature initial mixture of single bonds and olefinic double bonds became progressively aromatic and then graphitic as hydrogen is evolved.

A heating rate of 20 K/min is typical for TDS of thin *a*-C:H (for example see Refs. [10] and [11]) but also 60 K/min [12] and as much as 1200 K/min [13] were used for experimental purposes.

In a previous study [14], the PECVD of *a*-C:H films from pulsed discharges using five different hydrocarbons as precursors was investigated – mainly in view of their hardness and composition. To get additional information about the influence of the precursor on the structure of these films, thermal desorption mass spectroscopy was performed.

2. Experimental

The *a*-C:H films were deposited onto silicon substrates in a parallel-plate reactor using asymmetric bipolar pulsed discharges. Their frequency was varied between 50 kHz and 250 kHz (see Ref. [14]).

The precursors acetylene, isobutene, cyclopentene, toluene and cycloheptatriene were used in mixtures with argon. The thickness of the deposited films was measured with a surface profilometer Form Talysurf 50 (Rank Taylor Hobson). A nanoindentation system UMIS 2000 (CSIRO) equipped with a Berkovich-type diamond indenter tip was used to measure the hardness of the films. The thickness of films used for hardness measurements was above 1 μm to prevent any influence of the substrate. The total hydrogen content in the *a*-C:H films was measured by nuclear reaction analysis (NRA).

Thermal desorption was analysed in vacuum with a base pressure of the setup below 10^{-5} Pa.

A heating rate of 3 K/min was applied. Thus full analogue mass spectra in the range of mass numbers 1–100 u could be recorded at constant temperature steps of 17.5 K.

The quadrupole mass spectrometer (QMS) Dycor LC-D 100M (AMETEK) was operated at 70 eV electron energy and at the lowest possible electron emission current (0.1 mA) to minimize thermal modification of effusion products. To increase the sensitivity of the TDS analysis, the pumping of the chamber was optimized. By reducing the rotational speed of the turbo pump from 1500 Hz to 900 Hz, the sensitivity of TDS measurements could be drastically increased without approaching the upper pressure limit of the QMS operation. The mass-dependent sensitivity of the whole TDS system was measured using a calibrated mixture of rare gases (He, Ne, Ar and Kr) and absolute partial cross-sections for electron-impact ionization of these gases from the study by Rejoub et al. [15]. The measured QMS signals were corrected for the probed *a*-C:H film volume (normalised to 1 μm thickness and 1 cm^2 area). The gases H_2, H_2O, CO and CO_2 were released also with increasing rate when heating up the empty TDS sample holder. When analysing the thermal desorption from *a*-C:H, these continuous background signals were fitted and subtracted.

3. Results and discussion

The parameters varied during the deposition experiments [14] were the pressure, the gas flow ratios (precursor to argon), the frequency and the reverse time. For all precursors deposition at the lowest pressure of 2 Pa resulted in maximum film hardness. The hardness of *a*-C:H films deposited from the five precursors under very different process conditions behaves contrary to the total hydrogen content of the films (see Fig. 4 in Ref. [14]). That means, at a constant deposition temperature (100 °C) the total hydrogen content controls the hardness to a large extent.

When heated, the *a*-C:H films released mainly molecular hydrogen. Also the oxygen-containing gases H_2O, CO and CO_2 (but no O_2) were measured in substantive quantities. Since CO and CO_2 are again present when *a*-C:H films, after intermediate exposure to air, are analysed in a subsequent effusion experiment, their appearance is an indication of chemical reactions of *a*-C:H with water or oxygen [16]. The amount of evolved water molecules from hard *a*-C:H also in other studies exceeded the hydrocarbon signals [16,17], and water vapour is the second important gas.

Perhaps, just the water molecules may be responsible for that amount of hydrogen in *a*-C:H films which is not bound to carbon. Several attempts were made on the quantification of unbound hydrogen in diamond-like carbon films. Empirical, semiquantitative relationships have been derived to calculate the content of bound hydrogen in *a*-C:H films from the 2900 cm^{-1} IR band area [18], but the scatter of values is very large. In general, the measurement of the bound hydrogen fraction based on Fourier transform infrared spectroscopy (FTIR) [19] seems questionable, since the absorption strengths of individual C–H vibrations are not equal and they also depend on the film structure [11]. In a study by Pei et al. [20] the quantification of unbound hydrogen was based merely on elastic recoil detection analysis (ERDA) of the hydrogen content as a function of the annealing temperature. A reduced drop of the H content starting from 350 °C was attributed to a completed effusion of unbound hydrogen. For the analysed sample, the fraction of unbound hydrogen was estimated to be 22.6%. But the validity of these measurements is somewhat diminished, since they were not made on pure *a*-C:H but on TiC/*a*-C:H nanocomposite films, with titanium known to form hydrogen-rich hydride. The fraction of unbound hydrogen in *a*-C:H seems to be rather low. For *a*-C:H films deposited in DC plasmas from acetylene and cyclohexane the amount of hydrogen bound to carbon was found to be between 93% and 100% [21].

Analysing the films deposited using five precursors it was observed that with increasing film hardness the mass of the detectable hydrocarbon molecules decreased. The same trend for instance was observed in a study by Wild and Koidl [22]: films deposited at low bias ($|U_B| < 300$ V) released hydrogen, methane and higher hydrocarbons (detected by means of $C_2H_4^+$ and $C_3H_3^+$); medium bias films desorbed H_2 and CH_4 whereas from films deposited at $|U_B| > 500$ V only H_2 was released. In the study by Wild and Koidl [22] it was also experimentally demonstrated, that hydrocarbon diffusion is inhibited in hard/dense films by the reduced pore size of the strongly cross linked hydrocarbon network. But there are also opposite findings: the helium barrier efficacy of *a*-C:H coatings was found to decrease with an increase in film density [23]. This unexpected result was attributed to the formation of micro cracks at high intrinsic stress values. Not only the transport of species is hindered in hard films, but due to the lower density of CH_3 and CH_2 groups (sp^3 and sp^2 bound carbon) the thermally activated formation of higher hydrocarbons should also be reduced. The nature of the diffusing species – radicals or molecules – is discussed ambivalently. Delocalization of hydrogen atoms followed by surface recombination into hydrogen molecules was suggested as the mechanism of H_2 evolution [13]. In a study by Gerstenberg and Grischke [16] the formation of released molecules is considered to involve the thermally activated rupture of neighbouring bonds of network modifiers (–H, –CH_3) to the carbon