M. Šilinskas[a], A. Grigonis[b], Ž. Rutkūnienė[b], J. Maniks[c], V. Kulikauskas[d]

The Mechanical and Optical Properties of A-C:H Films Deposited from Acetylene Using Direct Ion Beam Deposition Method

[a]Institute of Micro-and Sensor Systems, Otto von Guericke University, Universitatsplatz 2, 39106 Magdeburg, Germany
[b]Physics Department, Kaunas University of Technology, 50 Studentu str., LT-3031 Kaunas, Lithuania.
[c]Institute of Solid State Physics, University of Latvia, 8 Kengaraga St.,Riga LV-1063, Latvia
[d]Nuclear Physics Institute, Moscow State University, 119899 Moscow, Russian Federation

Amorphous hydrogenated carbon (a-C:H) films were deposited from an acetylene/hydrogen mixture using a direct ion beam deposition method. The films were characterized by Raman spectroscopy (RS), Rutherford backscattering spectroscopy (RBS), ellipsometry, and microhardness measurements. The concentration of hydrogen increases with increasing hydrogen content in the deposition gas mixture. The hardness and the features of Raman spectra are dependent on hydrogen content and show a maximum of diamond-like fraction for a hydrogen to acetylene ratio of 1:1. Also, the strongest adhesion is observed for this gas mixture. Correlations are observed between the features of the Raman spectra and the hardness of the carbon films: the G and D bands shift to lower wave-number, the I_D/I_G ratio decreases, and the G band width at half maximum increases with increasing of film hardness.

Key words: amorphous hydrogenated carbon films, Raman spectroscopy, Rutherford backscattering spectroscopy, ellipsometry, microhardness

Introduction

Diamond-like carbon (DLC), both with and without hydrogen, has attracted increasing interest because of its outstanding properties such as high chemical resistance, mechanical hardness, wear resistivity and optical transparency in visible and IR light. The combination of these exceptional characteristics makes DLC films very interesting for a wide range of applications: protective coatings for magnetic recording media, top-surface coatings on sunglasses, wear resistant bar-code scanners, anti-reflection coatings for infrared optical lenses [1,2]. Those exeptional properties mainly depend on the structure of the material, resulting from a combination of four-fold coordinated sp^3 sites similar to diamond, and three-fold coordinated sp^2 sites as in graphite.

Robertson [3] proposed a cluster model, and predicted that amorphous carbon films consist of a three-dimensional network in which sp^2 islands are embedded. The range of these cluster sizes is large, but usually sp^2 islands are limited to single sixfold rings (aromatic) and short chains (olefinic). Graphite clusters determine the optical and electrical properties of the whole carbon film, while tetrahedral coordinated carbon atoms (sp^3 hybridized carbon) mainly determine the mechanical properties and allow a three-dimensional cross-linking, leading to the extraordinary hardness of the material [2].

However, the properties of plasma deposited a-C:H films depend not only on carbon sp^3/sp^2 bonding ratio but also on hydrogen content [4]. The hydrogen appears to play a very significant and different role as it can increase both C-C sp^3 and C-H bonding fractions [5-7].

In previous studies [8-10], we investigated a-C:H films, deposited from a mixture of hexane and hydrogen gases. We found that the optical properties of carbon films depend on the ion energy, the deposition temperature, and the amount of silicon or hydrogen. The best quality diamond-like films were formed at lower deposition temperatures and energies. We also found that the carbon film structure correlates with concentration of hydrogen molecules in the gas mixture at low (~ 15°C) temperature. This report presents further studies of the hydrogen influence on the optical and mechanical properties of carbon films deposited from acetylene.

I. Experiment

The a-C:H films were deposited on Si (100), Si (111) to a thickness up to 300 nm, by applying the direct ion beam deposition method at room temperature. Further details were reported elsewhere [10]. The films were formed by using pure acetylene gas or acetylene and hydrogen mixtures. The content of hydrogen gas in the mixtures was varied from 0 to 90%. The ion energy was

set to 1000 eV, the ion current density was about 0.12 mA/cm^2, the gas pressure was kept below 10^{-2} Pa. The deposition time was varied from 30 to 90 min.

The structure of the films was analyzed by RS. The Raman spectra were recorded by conventional grating Raman spectrometer. A argon ion laser, operating at 514,5 nm wavelength with 200 mW power, was used for excitation of the Raman spectra. Raman scattered light was collected using 90 degree scattering geometry. The laser beam was focused on the film by means of a 20 cm focal length glass lens. The temperature of the film in the illuminated area was slightly higher than room temperature. Raman spectra were recorded in the Raman shift range from 500 to 1900 cm^{-1}. The overlapped background corrected Raman spectral bands were fitted with two Gaussian contours, using least square fitting software.

The depth distributions of C and H atoms were measured by RBS using a 3,5 MeV ^{4}He^{+2} beam at a scattering angle of 170°. The concentrations of carbon or hydrogen atoms were calculated for a whole a-C:H film without surface (~ 10 nm) and film-wafer interlayer. The oxygen impurities were neglected.

The thickness and refractive index were measured using automatic rotating-polarizer ellipsometer (Gaertner L115) with He-Ne laser (632,8 nm).

The static microhardness measurements were performed using a loading device with a square-based Vicker's diamond pyramid as indenter. Vibration-damping allows accurate measurements for loads between 9,8 and 980 mN. The method is based on forcing the indenter under a constant load into the sample surface. The microhardness (H) is determined from the ratio of the applied load (P) and the projected area of the residual indentation by

$$H = 1,854 \ P/d^2.$$

The diagonal (d) of the indentation was measured by optical microscopy. The corresponding indentation depth (h) was estimated as one-seventh of the impression diagonal length. For each hardness data point, three impressions were made with a loading time of 15 s leading to an accuracy of about 5 %.

II. Results and discussion

Fig. 1 shows the hardness as a function of the indentation depth. This curve is characteristic to all a-C:H films. The first points indicate the hardness of the carbon films. These data are not absolute values for the a-C:H films because the influence of the substrate was not considered. The values at higher indentation depth are used for an evaluation of the adhesion to the silicon wafer by determination of the critical load of the peeling effect to occur. It was found that the film hardness varies from 16 to 25 GPa. The adhesion depends on the film thickness and hardness. The films with a lower thickness and higher hardness have better adhesion. For example, the films deposited with 50 % hydrogen show the highest hardness. When the thickness of these films is about 100 nm, there is no peeling for whole loading range (till 980 mN). But when the film thickness is about 200 nm,
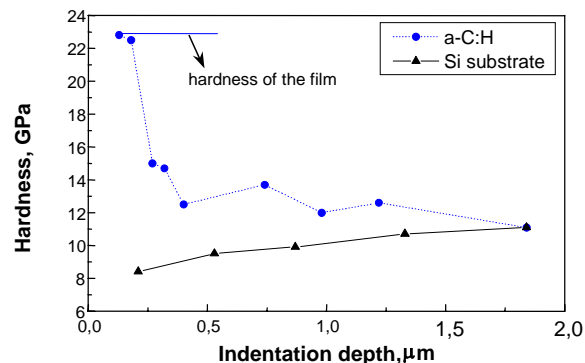

Fig. 1. Hardness of the a-C:H film and the silicon substrate as a function of the indentation depth. The a-C:H film was deposited from acetylene/hydrogen (1:1) mixture at room temperature.
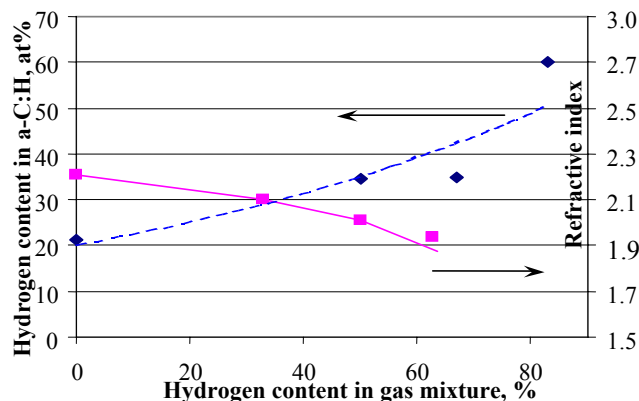

Fig. 2. Hydrogen concentration in the a-C:H films and refractive index of the a-C:H film as a function of the hydrogen content in the deposition gas mixture.

the film separates from the silicon wafer at 196 mN. The lowest film adhesion (critical loading – 98 N) was observed for thicker films deposited only with acetylene. One explanation for this effect could be the fact that the deposition rate for these coatings was the highest and a good adhesive substrate-film interface was not formed. It is also possible that stress and hardness do not correlate linearly and the highest stress is in the films that were deposited only with acetylene.

The hydrogen content and refraction index of the a-C:H films, deposited using various acetylene/hydrogen mixtures, are presented in Fig. 2. The increase of hydrogen (from 0 to 80 %) in the deposition gas mixture yields higher hydrogen concentration in the film (from 20 to 60 at%). The concentration of hydrogen in the film is extremely high (60 at%) for the 80 % hydrogen gas mixture. In this case, the thickness of the carbon film was only 15 nm and surface and interface layers had higher influence to elemental composition of the film. Otherwise, the highest refractive index (2,71) is observed for films deposited without hydrogen. The refractive index decreases with the increasing of the hydrogen ratio in the deposition gas mixture over the whole hydrogen concentration range. The lowest refractive indexes (2,05) are observed when the hydrogen content in the deposition gas mixture exceeds 67 %. The hydrogen

concentration and refractive index are closely correlated and the tendency of a decreasing refractive index is related to the formation of a less dense network because of the higher hydrogen content in the film [11]. Schwarz-Selinger et al. [4] found a correlation between the index of refraction and the hydrogen fraction in the a-C:H, deposited by plasma CVD. From these data, we can estimate that our films, deposited without additional hydrogen, have < 5-8 at% hydrogen. The a-C:H films with the lowest (2,04) refractive index have about 35 at% hydrogen. The RBS data show a slightly higher hydrogen concentration. A good agreement between RBS and ellipsometry measurements is observed in the range of high hydrogen concentration. In the case of the deposition without hydrogen, the difference reaches 10 at%. We should note that Schwarz-Selinger correlation was obtained for lower refraction index range (from 2,5 to 1,6) and might be not valid for higher refraction indexes.

The curve of hardness shows a different behavior than the curves of refraction index, and hydrogen concentration, respectively (Fig. 3). The hardness passes through a maximum as a function of hydrogen concentration in the feed gas mixture. The maximum of the hardness (~ 24 GPa) is observed at 50 % hydrogen in the deposition gas mixture. When no hydrogen was used the hardness falls to the minimal value (only ~ 16 GPa). A decrease of the hardness is also observed for the films deposited with higher than 50 % fraction of hydrogen. The increasing of hardness means that the number of the sp^3 C-C bonds is also increased at low hydrogen concentration because the mechanical properties are determined by sp^3 C-C bonds. However, the fraction of C-H bonds also increases. C-H bonds do not contribute to film hardness because they only terminate the network. When the concentration of hydrogen is too high, it reduces the three-dimensional inter-links in the atomic bond network. As a result, the hardness decreases at higher hydrogen content.

Figure 4 shows the changes in the Raman spectra as a function of the hardness for the films deposited at various hydrogen contents (from 0 to 67 %). It was not possible to obtain meaningful Raman and hardness data for films, that were deposited with a hydrogen concentration of more than 67 %, because film thickness was not sufficient for microhardness measurements and for reasonable signal to noise ratio in the Raman spectra. However, good correlations between the film hardness and the features of Raman spectra are found. The G and D bands are situated at ~1542 and ~1322 cm^{-1} and the I_D/I_G ratio is lowest (~ 0,6) for the hardest (≥ 24 Gpa) a-C:H films, which are deposited with 50 % hydrogen concentration in the deposition gas mixture. Such deposition conditions also lead to the highest broadening (up to ~ 160 cm^{-1}) of G band. The D spectral band appears as a weak shoulder in the total spectral band and fitting does not give reliable values for the band width, therefore this band width was not used for the analysis. The D and G bands shift to higher wave-numbers, the G width decreases, and the I_D/I_G ratio increases with decreasing of the film hardness. These changes have the same character for films deposited with both higher
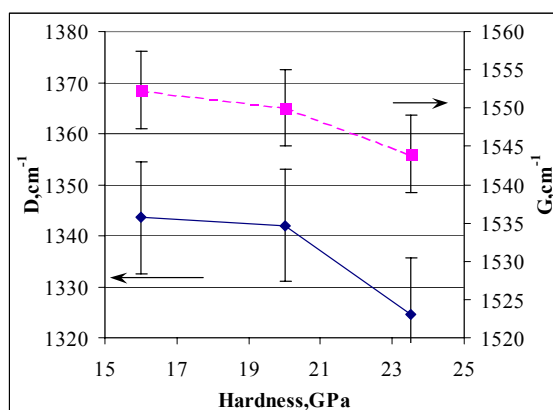

Fig. 3. Hardness of the a-C:H films as a function of the hydrogen content in the deposition gas mixture.

(> 50 %) and lower (< 50 %) hydrogen contents.

The visible RS is related primary to the graphite phase, but the shifting of D and G bands toward lower wave-numbers indicates an increasing of the sp^3/sp^2 bonding ratio for the hydrogenated carbon [12]. The broadening of the G band and the reducing of the I_D/I_G ratio with increasing hardness indicates lower sp^2 islands size and worse order (bond lengths and angles) in these graphite clusters. The hardest films show less graphitic Raman spectrum, and overall less graphitic behavior. Ferrari et al. [12] gave a graphical relation for both the G
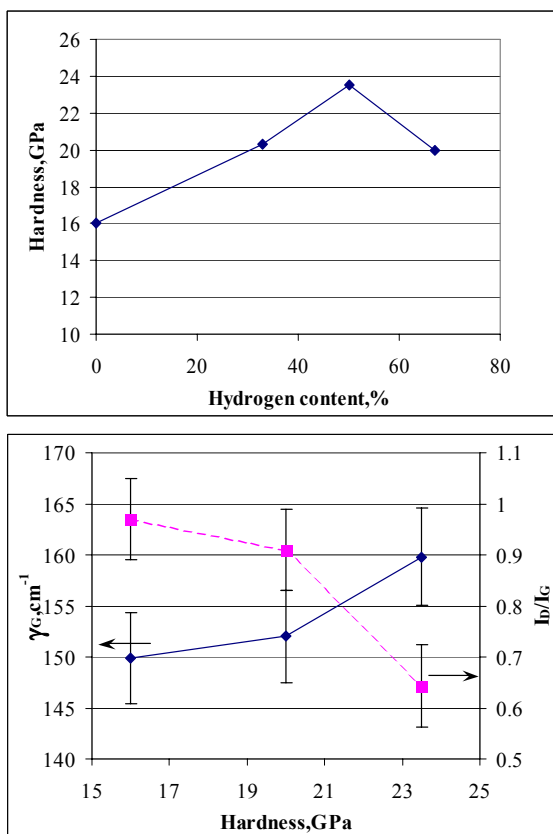

Fig. 4. Variation of the Raman features as a function of hardness. (a) Variation of the G and D peak centers. (b) Variation of the G band width and the I_D/I_G ratio.

band position and the I_D/I_G ratio as a function of the sp^3 content. This relation was obtained for 514 nm laser light, with Gaussian fitting, and only for hydrogenated carbon films. We should note that the I_D/I_G ratio gives a little higher (~ 5 %) sp^3 content than the G peak position. In our case, the hardest (~ 24 GPa) carbon films have 40-45 % sp^3 bonds, the softest – 30-35 %. This means that amount of sp^3 bonds defined by RS is proportional to the number of sp^3 C-C bonds and this statement is valid for the whole hydrogen content range.

Conclusions

In this work, we have studied the mechanical and optical properties of the a-C:H films by RS, RBS, ellipsometry, and microhardness measurements. We found correlations between the hardness, the features of Raman spectra, the hydrogen fraction in the film, and thehydrogen concentration in the deposition gas mixture. The concentration of hydrogen in the film increases from ~ 20 to 40 at% and the refractive index decreases from $\sim 2,7$ to 2,0 with increasing of the hydrogen content from 0 to 67 % in the gas mixture. A maximum of hardness (≥ 24 GPa) and a maximum of sp^3 bonds ($\sim 40-45$ %) defined by RS were observed when the hydrogen to acetylene ratio in the deposition gas mixture was 1:1. The properties of a-C:H films became more graphite-like when the content of hydrogen was more or less 50 %.

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М. Сілінскас[a], А. Грігоніс[b], З. Руткунене[b], Й. Менікс[c], В. Кулікаускас[d]

Механічні і оптичні властивості осаджених з ацетилену плівок А-С:Н, з використанням методу направленого бомбардування йонами

[a]Інститут мікро- та сенсорних систем, Магдебург, Німеччина
[b]Каунаський технологічний університет, вул. Студентська, 50, LT-3031 Каунас, Литва.
[c]Інститут фізики твердого тіла Латвійського університету, вул. Кангарага, 8, Рига LV-1063, Латвія
[d]Московський державний університет, Інститут ядерної фізики, 119899 Москва, Російська Федерація

Аморфні гідровані вуглецеві плівки (а-С:Н) наносили із суміші ацетилену / водню, із використанням прямого методу осадження йонного пучка. Плівки досліджували Раманівською спектроскопією (RS), Резерфордівською йоннорозсіюючою спектроскопією (RBS), еліпсометрією та вимірюванням мікротвердості. Концентрація водню збільшувалася із збільшенням його вмісту у газовій суміші осадження. Твердість і особливості Раманівських спектрів залежать від вмісту водню і показують максимум алмазоподібної долі для водню у співвідношенні ацетилену 1:1. Для цієї суміші спостерігається найбільш сильна адгезія. Кореляції спостерігаються між особливостями Раманівських спектрів та твердості вуглецевих плівок: Г і D зони переміщуються, щоб понизити хвильове число, зменшується співвідношення ID/IG та ширина зони Г у зростанні наполовину максимума із збільшенням твердості плівки.