Investigation of ultrathin carbon film growth and etching by in-situ X-ray reflectivity

A M Baranov and I I Ivanov

1 Moscow Aviation Institute (National Research University), Moscow, Russia
2 LLC "NTC IGD", Lyubertsy, Moscow Region, Russia

E-mail: baranov_64@mail.ru

Abstract. The results of studies of carbon films in the process of their growth and etching in plasma of radio-frequency discharge in real time by in-situ X-ray reflectometry are presented. The film thickness, growth rate, density and surface roughness were calculated from the time dependence of the reflection coefficient of x-rays at a wavelength of 1.54 A. A method for the production of carbon films with a super-smooth surface was proposed.

1. Introduction
It is known that carbon films are distinguished by exceptionally high mechanical and tribological characteristics, biocompatibility, as well as chemical inertness and corrosion resistance [1]. Recently, it has also been suggested that amorphous carbon films are promising material for memory based on phase transition (PCM) and resistive random access memory (RRAM) [2]. Amorphous carbon can be considered as a universal material for electrochemical electrodes [3].

The variability of the properties of carbon films is an attractive fact, because it allows the formation of layers with the desired properties. However, this circumstance complicates their practical use, since a small change in any technological parameter during the growth process can lead to a strong change in both the structure and, consequently, the properties of the growing film, and the growth rate of the film. This causes the urgent need to change the traditional approach in monitoring the parameters of carbon films and, in particular, the development and use of new diagnostic methods in the technology of thin carbon films, allowing continuous measurement of film parameters in the process of their synthesis (in-situ measurement).

In this work the parameters of ultrathin a-C:H films in the process of their growth and etching in plasma of radio-frequency discharge were investigated by in-situ X-ray reflectivity.

2. Experimental
The a-C:H films deposition were carried out by RF-plasma-enhanced chemical vapor deposition (PECVD) in C6H6+Ar mixtures (f=13.56 MHz) at room temperature. The etching of a-C:H films was performed by RF reactive ion etching in the same system. Oxygen was used as etching gas. During deposition and etching in RF-system, DC bias on the substrate was about –120 V and –180 V, respectively. In-situ measurements of the thickness (d), surface roughness (σ) and density (ρ) of film were carried out by means of the X-ray optical system (figure 1(a)).

The in-situ X-ray reflectivity method is based on the interference of X-rays reflected from the vacuum-film and film-substrate interface during the film thickness changes [4]. In essence, the in-situ
X-ray reflectivity method is close to laser interferometry. However the use of a wavelength of 1.54 Å allows one to investigate the growth of films starting from 10 Å. At the same time, besides the film thickness, the film density and the surface roughness could be also measured that are extremely important for ultra-thin films.

Angle of X-ray incidence Θ = 1°. The silicon wafers with initial root mean square roughness of surface σ=8 Å were used as a substrates.

**Figure 1.** Schematics of the deposition chamber with the X-Ray Reflectivity system used to real time monitor the film growth (a): 1 – vacuum chamber; 2 – gas system; 3 – to the pumping system; 4 – substrate; 5 – substrate holder; 6 – electric motor; 7 – RF-generator; 8 – Be windows; 9 – X-ray tube; 10 – X-Ray detector; 11 – controller; 12 – computer; 13 – slit. The time dependence of X-ray reflectivity during the deposition of carbon film (curve 1) and its etching (curve 2) (b): Std – the beginning of deposition; Spd – the end of deposition; Ste – the start of etching.

A change in the film thickness (d) leads to periodic oscillations of the reflection coefficient (figure 1(b)). The repetition period of oscillations (L) is determined by the Bragg equation [5]. A change in the density and surface roughness of the film leads to a change in the amplitude of the oscillations and their average value. Therefore, analyzing the shape of the experimental dependence I(t), one can calculate the values of density (ρ) and surface roughness (σ) directly in the process of film growth [4].

**Figure 2.** The calculated values of the surface roughness of the film (a) and its density (b) during deposition (curve 1) and etching (curve 2).
Figure 1(a) (curve 1) shows the experimental dependence of the intensity (I) of the reflected beam on the deposition time of the carbon film I(t) on a silicon wafer. It can be seen that the dependence I(t) oscillates as the film grows. After the growth process is completed, the oscillations of I(t) are not observed. The growth rate (V) is calculated by the formula \( V = \frac{L/2}{(t_{m+1} - t_m)} \) (where \( t_m \) is the time corresponding to the extrema \( m = 1, 2, ... \)), the film thickness is \( d = \frac{L}{2} \times m + V(t_i - t_m) \) (where \( t_i \) is the current time). On the same figure 1(b) (curve 2) shows the dependence of the intensity of the reflected beam on the system of silicon-carbon film in the process of etching the film. Etching occurred in an oxygen plasma excited by an RF voltage. It is obvious that the etching (curve 2) repeats the deposition process, but goes above the first one and changes with a much lower speed. The disappearance of oscillations indicates the complete removal of the film from the substrate surface and allows determining the end of the etching process.

The \( \sigma \) and \( \rho \) dependences calculated on the basis of the curves of the film deposition and etching (figure 1(b)) are presented in figures 2(a) and 2(b). It is seen that with the growth of the film there is an increase in density and roughness from 1.53 g/cm\(^3\) to 1.9 g/cm\(^3\) and from 8 A to 9 A, respectively. With a film thickness of more than 120 A, its density and roughness remain almost unchanged. On the contrary, in the etching process with a decrease in the film thickness to 66 A, its density does not change.

3. Results and discussion

Studies have been conducted of the dependence of the growth rate of carbon films on the pressure of cyclohexane and the Ar content in the gas mixture Ar+C\(_6\)H\(_{12}\). The dependences obtained are shown in figure 3.

![Figure 3](image-url)

Figure 3. The dependence of the growth rate of carbon films on the pressure of C\(_6\)H\(_{12}\) (a), the dependence of the growth rate (b) and the surface roughness of the film (c) on the pressure of Ar in the mixture of C\(_6\)H\(_{12}\)+Ar. The pressure of C\(_6\)H\(_{12}\)=2.6*10\(^{-2}\) Torr (curve 1) and 5.8*10\(^{-2}\) Torr (curve 2).

From figure 3(a), it can be seen that, in the region of low pressures, the growth rate of films increases sharply from 3.1 A/s to 7.8 A/s with increasing pressure C\(_6\)H\(_{12}\). Having reached the maximum value at \( P=2.6*10^{-2} \) Torr, the growth rate slowly begins to decrease to 5.5 A/s with increasing pressure to \( P=5.8*10^{-2} \) Torr.
The addition of Ar at a constant pressure of cyclohexane led to a decrease in the growth rate of the films. Apparently, due to the sputtering of a growing carbon film with Ar ions. Two dependencies were obtained at a partial pressure of cyclohexane \(2.6 \times 10^{-2}\) Torr (figure 3(b), curve 1) at which the growth rate of the carbon film is maximum and at \(5.8 \times 10^{-2}\) Torr (figure 3(b), curve 2). It is seen that with a pressure of cyclohexane \(5.8 \times 10^{-2}\) Torr the growth rate changes only slightly with increasing partial pressure Ar. At that time, as with a cyclohexane pressure of \(2.6 \times 10^{-2}\) Torr (figure 3(b), curve 1), the growth rate decreases twice as the partial pressure Ar increases to \(3.6 \times 10^{-2}\) Torr, and then remains virtually unchanged. A stronger decrease in speed with a pressure of cyclohexane \(2.6 \times 10^{-2}\) Torr can be explained by two circumstances: the fact that the negative bias voltage on the electrode on which the substrates were located is about two times higher (\(~\approx 200\) V) and the fact that the percentage of Ar in the gas mixture is higher. As a result, the sputtering rate of a growing film with Ar ions will be higher.

Confirmation of the fact that Ar ions are sputtering a growing carbon film is a change in the surface roughness of the film at a pressure of cyclohexane \(2.6 \times 10^{-2}\) Torr (figure 3(c), curve 1) and the practically unchanged value of roughness at a pressure of cyclohexane \(5.8 \times 10^{-2}\) Torr (figure 3(c), curve 2). The density of films in all cases remained almost unchanged.

4. Conclusions

It was shown that the growth rate of ultrathin a-C:H films, density and surface roughness can vary greatly depending on both the deposition conditions and during film growth. Using the method of in-situ X-ray reflectometry allows one to monitor the parameters of a-C:H films and control the deposition technological process.

As can be seen from figure 2(a), the surface roughness of the carbon film is less than the roughness of the initial silicon wafer (except for the layers near the Si substrate) during etching in oxygen.

Reducing the surface roughness of the carbon film is extremely important because it allows to obtain carbon films with a super-smooth surface. Besides, it is possible not only to obtain carbon films with a super-smooth surface, but also to reduce the surface roughness of other materials and functional layers. The method of planarization will consist in deposition of a thin carbon film on a material surface and then carrying out the ion-plasma polishing etching of carbon film. As a result we obtain the substrate with the carbon film in which the surface roughness is less than that of the substrate itself. It is important to note that carbon films are rather easily polished in an RF plasma in oxygen and the carbon film thickness can be only several dozens of angstroms.

The observed effect of reducing the surface roughness of carbon films can be used to reduce the friction of the carbon of coatings [6, 7], increase the reflection coefficient of X-ray mirrors [8], and also activate clusters of catalytically active metals (Pt, Pd, Ag) included in carbon nanocomposites functional layers [9, 10].

References
[1] Alotaibi S, Manjunatha K N and Paul S 2018 *Diamond & Related Materials* **90** 172–80
[2] Kun Ren, Yan Cheng, Xin Chen , Keyuan Ding , Shilong Lv, Weijun Yin, Xiaohui Guo, Zhenguo Ji and Zhitang Song 2017 *Materials Letters* **206** 52–5
[3] Medvedeva E, Baranov A and Somov A 2016 *Sensors and Actuators B: Chemical* **236** 858–4
[4] Baranov A M and Mikhailov I F 1998 *Thin Solid Films* **324** 63–7
[5] Spiller E 1994 *Soft X-ray Optics* (SPIE Optical Engineering Press)
[6] Baranov A M 1998 *Surface and Coatings Technology* **102** 154–8
[7] Matlak J and Komvopoulos K 2015 *Thin Solid Films* **579** 167–3
[8] Chkhalo N I, Gaikovich P K, Salashchenko N N, Yunin P A and Zuev S Yu 2016 *Thin Solid Films* **598** 156–60
[9] Medvedeva E, Klochkova E, Kondelinskaya T, Baranov A and Somov A 2015 *Procedia Engineering* **120** 1137–40
[10] Medvedeva E A and Baranov A M 2018 *IOP Conference Series: Materials Science and Engineering* **387** 012052