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XPS and Auger study of the radial variations of diamond thin films grown by the oxy-acetylene flame method

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Abstract

Free standing diamond thin films grown by the oxy-acetylene flame method have been investigated by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). The radial distribution of the sp^2-hybridized carbon species on the films and, consequently, the film quality, have been determined. While XPS does not seem to be an appropriate technique to distinguish between very small variations in film quality, an analysis of the Auger widths can explain the differences observed by scanning electron microscopy (SEM) and optical microscopy in the different regions of the samples.

Keywords: X-ray photoelectron spectroscopy; Auger electron spectroscopy; Diamond thin films

1. Introduction

Diamond production is a highly interesting topic due to the unique properties of this material, such as its high thermal conductivity, very high wear and chemical resistance, good optical and mechanical properties, and wide band gap. These properties make diamond a very suitable material for many technological applications. As a consequence, several techniques to obtain diamond or diamond-like films have been developed, most of which involve chemical reactions of molecules in the gas phase in the so-called chemical vapour deposition (CVD) [1–4]. Most of these techniques require different vacuum conditions and the chemical reactions involved take place at low pressures. The recently developed oxy-acetylene flame method, however, produces high quality diamond films at atmospheric pressure with a very simple and low-cost experimental set-up [5–8]. Growth rates as high as 50 μm/h have been reported using this technique [5], in which diamond is produced in the non-oxidant zone of the flame. In this region acetylene is partially oxidized, which gives a similar composition to that of a plasma at temperatures of 3000 K. The use of flat flames [9,10] or multiburners [11] can lead to some improvement in the quality of the films and a larger exposed surface.

The quality of the diamond films is determined by the extent of the different reactions taking place in the production of the films. These reactions produce diamond and other forms of carbon (usually amorphous), and they are responsible for morphological differences in the diamond crystals and change the amount of amorphous carbon present in the films [12–14]. These differences are present in different areas of the same film when the deposition conditions are not homogeneous. With the oxy-acetylene flame method there is a radial gradient of flame composition and substrate temperature, which together with a difference in the turbulence conditions produce a radial distribution in the morphology and composition of the films [14,15]. A number of methods can be used to study these changes, such as Raman spectroscopy, X-ray diffraction, electron-energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), etc. [15–18]. XPS and AES have been used in this work to characterise free-standing diamond films produced by the oxy-acetylene flame method on a Mo substrate. AES spectra show a radial dependence of the quality of the films, which is discussed and compared to the corresponding morphology observed by scanning electron microscopy (SEM) on the same films.

2. Experimental procedure

Acetylene combustion was performed with a commercial No. 2 welding torch with oxygen and acetylene rates

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controlled with a mass flow control system, model UNIT 1100, with total flow of 3 slm. The substrates consisted of molybdenum threaded rods, 15 mm long and 8 mm in diameter, inserted in a water-cooled copper block. This is done in order to control the substrate temperature. The temperature was determined with an optical-infrared pyrometer, model IMPAC IS2. Substrate surfaces were polished prior to deposition with diamond paste and subsequently cleaned with trichloroethylene, acetone and methanol to remove possible contamination during the polishing process. A complete description of the set-up can be found in Ref. [8].

Several diamond films were deposited with O_2/C_2H_2 molar ratios ranging between 0.93 and 0.99. If the molar ratio was lower than 0.8 the films produced had a large amount of amorphous carbon and was of a much lower quality. On the other hand, if the molar ratio was higher than 0.98 the quality of the films was increased, although their area was decreased. Deposition times varied from 20 to 30 min, resulting in an average thickness of the films between 5 and 6 μm. Mo surfaces were 1.5 mm away from the tip of the reaction cone of the flame. The low rugosity of the Mo surface (<0.1 μm) allows a high nucleation density, so a very thin continuous diamond film is obtained after only 2 min. Quenching the samples to room temperature produces delamination of the diamond films due to the different thermal expansion coefficients of diamond and molybdenum. Diamond films detached from the substrate were adhered with silver glue onto a metallic support and characterized with the techniques mentioned above.

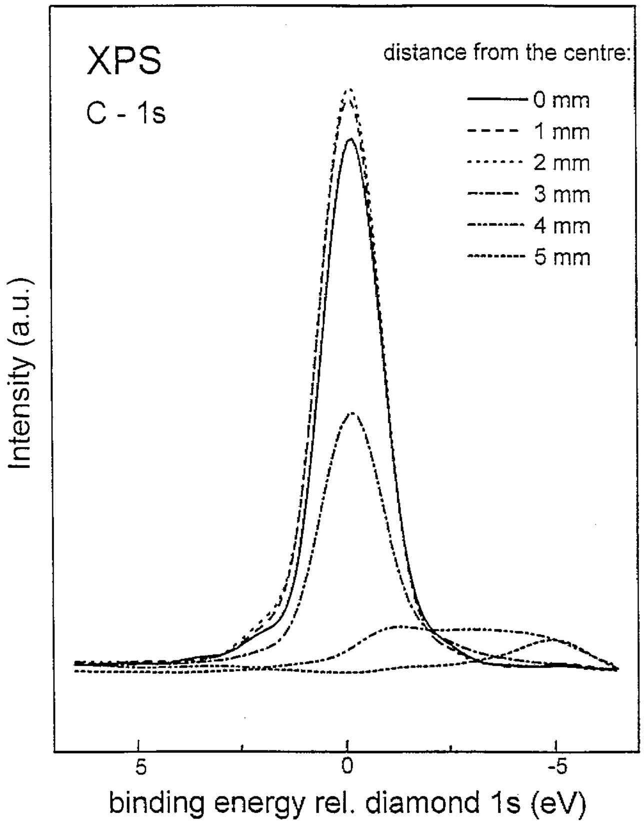


Fig. 1. C 1s XPS spectra of a CVD diamond thin film grown by the oxy-acetylene flame method with an O_2/C_2H_2 molar ratio of 0.97, a substrate temperature of 950°C, and a deposition time of 20 min. The different spectra correspond to different positions with respect to the sample centre; 4 and 5 correspond to zones outside the diamond film.

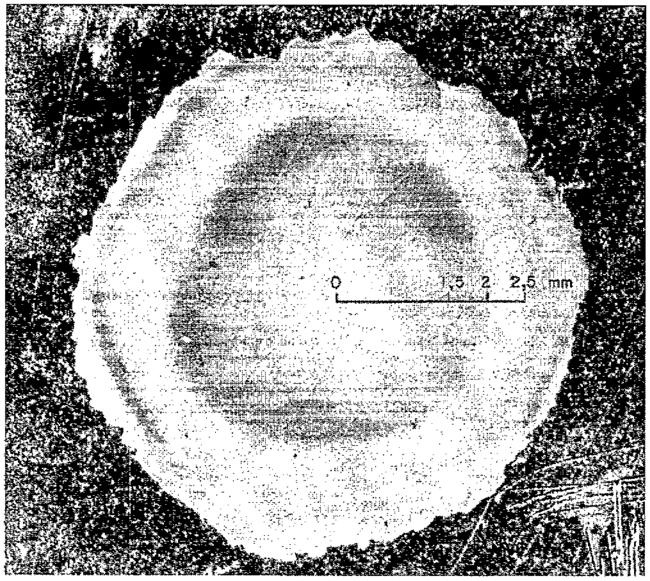
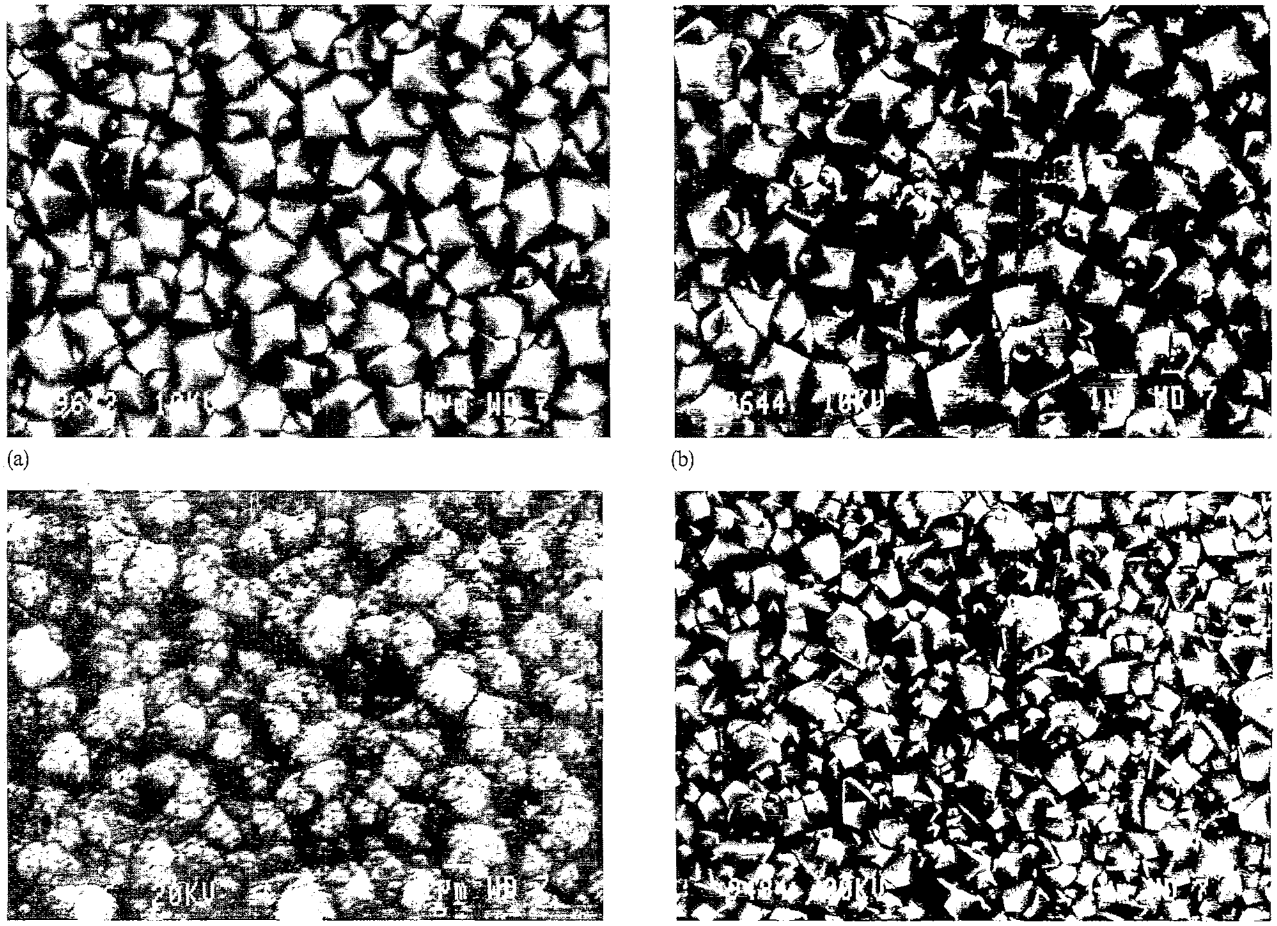


Fig. 2. Macrograph of a CVD diamond film with an O_2/C_2H_2 molar ratio of 0.97, a substrate temperature of 950°C and a deposition time of 20 min.

SEM images were taken in a high vacuum chamber with a commercial JEOL microscope. XPS and Auger spectra were recorded under ultra-high vacuum (UHV) conditions with a VG-CLAM hemispherical electron-energy analyzer equipped with a special lens to probe small areas on the sample (<1 mm^2). Additionally, an electron gun with a spot size of 50 μm and 3 keV acceleration energy was used as an excitation source for the Auger spectra. The base pressure in the UHV-chamber during the measurements was better than 1×10^{-9} mbar. The energy resolution for the XPS spectra was set to ~0.4 eV. Samples were not subjected to any cleaning process inside the UHV-chamber since it was noted that ion sputtering leads to graphitization of the surface of the diamond film [16].

3. Results and discussion

Fig. 1 shows C 1s XPS spectra of a diamond film grown by the oxy-acetylene flame method with a O_2/C_2H_2 molar ratio of 0.97, a substrate temperature of 950°C, and a deposition time of 20 min, taken at several positions with respect to the centre of the sample. An energy shift of ~200 meV is expected between the C 1s core level of graphite and diamond [18]. Although the



(a) (b)

(c) (d)

Fig. 3. SEM micrographs of different zones of diamond films similar to that shown in Fig. 2: (a) central part; (b), (c), and (d), at 1.5, 2–2.5 and >2.5 mm from the centre of the film. Images (a), (b), and (d) correspond to a film with a molar ratio of 0.97 and (c) to another film with a molar ratio of 0.93.

energy resolution does not allow to resolve such a difference, a lineshape analysis can serve as a first approximation to estimate the radial variation of the film quality. An increase in the amount of graphite or amorphous carbon concentration would be indicated by a shoulder or an asymmetry at the lower binding energy side of the spectrum [19]. This is indeed the case for the spectrum taken at 3 mm from the centre, where a small asymmetry is observed at the right hand of the peak. This asymmetry is not present in the spectra taken at shortest distances from the centre, or in that at the central position (labelled 0, 1, 2, and 3 mm), which suggests that the quality of the film is homogeneous to this distance. At 4 mm from the centre, the diamond peak has almost disappeared and a double structure is clearly visible. The higher binding energy component originates from the almost exclusively graphitic character of the edge of the film, whereas the lower binding energy component is due to the carbon-containing silver paint beyond the edge of the film. Note that the size of the probed area is ~1 mm^2, so that three regions are being at looked simultaneously: a very small part of the diamond film, the edge, and the region beyond the edge where the silver paint is present. The energy positions of each of the peaks observed by XPS might not be reliable due to possible charge effects in the diamond film, but serve to distinguish between the different components.

Although XPS can serve as a first approach to estimate the quality of the films and to determine the amount of graphitic or amorphous carbon in comparison to diamond, its sensitivity is not high enough to allow a description of films with very high quality, like those grown with the present method. Fig. 2 shows an optical macrograph of a diamond film delaminated from the Mo substrate (free-standing). This film was made with a O_2/C_2H_2 molar ratio of 0.97, an average substrate temperature of 950°C, and a deposition time of 20 min. Several regions can be observed on the surface of the film, seen as different grey areas. The inner, almost circular region, has a radius of approximately 2 mm, and corresponds to the region exposed to the central

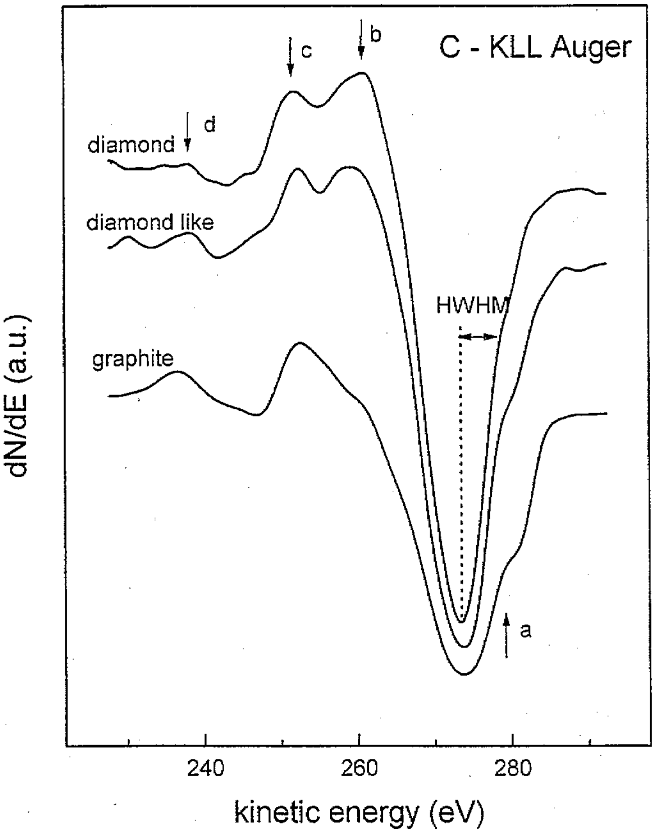


Fig. 4. Carbon-KLL Auger spectra in derivation mode of diamond, diamond-like carbon and graphitic carbon grown on a molybdenum substrate. While features a and d are characteristic of graphite, feature b relates to the sp^3 bonding in diamond. Note the larger width of the derivative peak in the case of graphite as compared to diamond.

part of the acetylene plume, where there is no oxygen from the atmosphere (or a very small amount); this gives the best diamond quality. A small colour gradient is, however, observed from the central, lighter part to the darker edge. Some cracks are also visible all over this first region; they are a consequence of the rapid quenching to room temperature after deposition, and indicate a homogeneous crystallinity of the film in this region, assuming intergranular fracture [20]. The second region corresponds to the ring-shaped, lighter area surrounding the central part. Its width varies between 0.5 and 1 mm. The fact that no cracks are observed in this region involves a lower crystallinity than the central region. Finally, a third region can be observed after this halo, close to the edge, with a slightly brighter colour than the central region. In order to be able to assess fully the variation of the quality of the film with increasing distance from the centre, it is necessary to carry out a more detailed analysis, because the change in shades of grey of the film only gives a rough estimation of the quality (as well as that of the change in thickness of the film).

Fig. 3 shows radial differences that are not observed in the XPS data. In Fig. 3, SEM images taken at different positions with respect to the centre of the film are shown. Fig. 3(a) corresponds to the central point, where the film has the best quality. This can be seen in the homogeneous size of the crystals as compared to those shown in Fig. 3(b), corresponding to the darker area of the central region indicated in Fig. 2, where secondary growth can be observed. When the amount of amorphous carbon in the film increases, new nucleation sites are created and small-sized crystals start to grow in a competitive process with the enlargement of the previous ones. This mechanism is known as secondary growth and gives an estimate of the amount of amorphous carbon present in a diamond film. Fig. 3(c) corresponds to the white halo surrounding the central region, which has a much lower quality as it can be seen by the lack of faceted crystals. Finally, Fig. 3(d) shows the SEM image of the outermost region of the film, where the quality increases again, although secondary growth like that shown in Fig. 3(b) can be observed.

In view of the small size of the different regions observed in the diamond films (Fig. 2 and Fig. 3) a microfocus technique is needed in order to characterize them properly. The probed area size in XPS was ~1 mm^2, which is not small enough to determine the differences between the regions. As a matter of fact, the XPS spectra suggest the existence of a homogeneous region with a radius close to 3 mm (see Fig. 1) which, according to Fig. 2 and Fig. 3, is not realistic. In Fig. 4 we show carbon KLL Auger spectra for diamond, diamond-like carbon, and graphitic carbon. Diamond-like carbon means polycrystalline diamond with a visible content of interstitial sp^2 carbon. The spectrum labelled "graphite" corresponds to an evaporated film on Mo. Both diamond and graphite spectra show very well-defined features similar to previously reported data [21–24]. Features labelled a, b, and d are fingerprints of the different hybridizations of the valence states in graphite and diamond. Features a and d are associated to the sp^2-hybridization of graphite or amorphous carbon, whereas feature b is related to the sp^3 hybridization of diamond. Additionally, the width of the main peak is also different for diamond and graphite, the half width half maximum (HWHM) in the case of graphite being much larger than in the case of diamond (8 and 5 eV, respectively). Whilst the presence or absence of features labelled a–d in the Auger spectra permit a qualitative characterization of the sample to be studied, a quantitative analysis based on the width of the main peak is also possible [24]. Such analysis has been performed on two samples with molar ratios 0.93 and 0.97 in order to characterize the different regions observed in Fig. 2 and Fig. 3. The result is shown in Fig. 5, where the HWHM vs. distance to the centre is shown. In this case the lateral resolution of the electron gun was 50 μm, much smaller than for XPS, so the results are better justified in this last case. The large error bars are originated by charging effects due to the insulating character of the diamond films, that produce shifts of the Auger peaks leading to small differences in the corresponding width. A lower value of the HWHM indicates a better quality of the diamond film, i.e., a smaller content of sp^2-hybridized carbon. Though both samples present a very high quality, the sample grown at a molar ratio of 0.97 shows a better behaviour at any position than that grown at 0.93, as already expected. In both cases a similar trend is observed with respect to the position, the central region being that with the best quality. The external, darker part of the central region (see Fig. 2) has a slightly larger width in the case of the sample grown at 0.97, while for that grown at 0.93 it remains approximately constant. The region corresponding to the white halo, located between 2 and 3 mm away from the centre, is the one with the highest amorphous carbon content, as has already been inferred from Fig. 3(c). This figure shows a film deposited with a molar ratio of 0.93, instead of 0.97. For the most external region, the dark area close to the edge, the quality is similar to that at 1–1.5 mm from the centre (Fig. 3(a) and Fig. 3(d)).

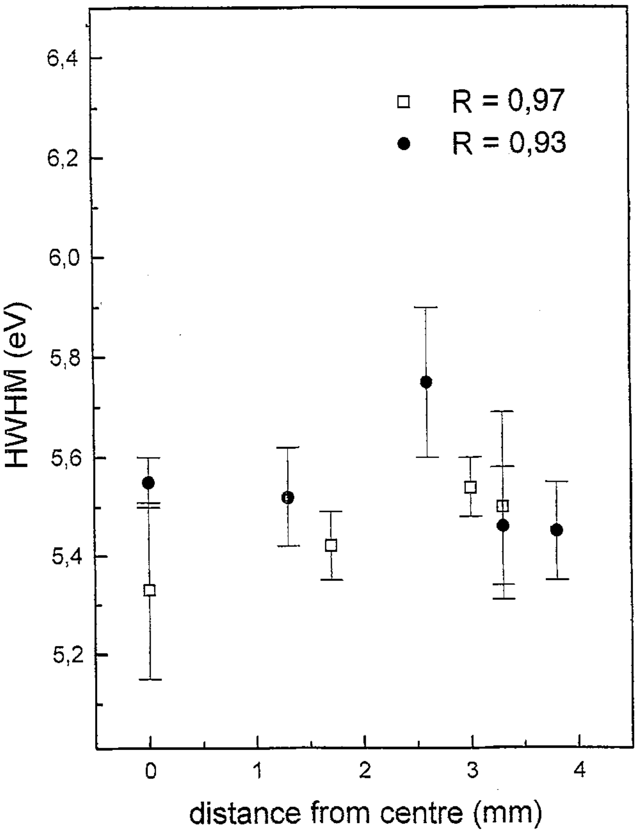


Fig. 5. Dependence of the HWHM of the C-KLL Auger peak upon the position of the incoming electron beam with respect to the film centre for O_2/C_2H_2 ratios of 0.93 (black circles) and 0.97 (open squares). In both cases the substrate temperature was 950°C and the deposition time 20 min.

The amount of non-diamond carbon in the film, as well as its morphology, relates to the amount of etching species present in the flame [25–28]. These species remove the sp^2-hybridized carbon atoms at a much faster rate than the more tightly bound diamond atoms and, consequently, there is a net growth of diamond. Although a lot of different chemical reactions and species are involved in this etching process and the mechanisms are complicated, the presence of oxygen is essential in the formation of the chemical etching agents [25,26]. A low oxygen concentration implies a lower content of etching radicals in the flame (OH or CO) and, consequently, a worse quality of the diamond film. In our case, the best diamond quality corresponds to the film grown with the highest oxygen ratio, i.e., 0.97. A second important factor in the quality of the films is the temperature of the substrate. When the distance to the central point of the flame increases, the quality decreases; slowly near the centre and faster as the distance to the centre increases (see white halo shown in Fig. 2). These changes are associated to the temperature gradient of the substrate, which has a similar dependence [13]. The most external part of the film, however, changes this trend and the quality improves. Similar results using Raman spectroscopy have already been reported [13]. To explain this phenomenon one has to take into account the oxygen diffusion from the outside takes part in the combustion of the outer part of the flame. This increases the amount of etching agents and, consequently, the quality of the film in the external region. The contribution of oxygen in the combustion and film quality is suggested by the good correlation between the HWHM data extracted from the Auger spectra and the evolution observed in the SEM images of Fig. 3.

4. Conclusions

Diamond thin films grown by the oxy-acetylene flame method with O_2/C_2H_2 molar ratios of 0.93 and 0.97 have been investigated by XPS, SEM and AES. The XPS data show that all the films have good quality, but they cannot explain the radial differences in morphology observed by SEM and optical microscopy. On the other hand, an analysis of the HWHM of the C-KLL Auger peak taken at different positions on the films gives a good correlation with the morphological differences observed by SEM and can be used as an indication of the changes in films of high crystalline quality.

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