

# Nucleation of diamond on silicon, SiAlON, and graphite substrates coated with an *a*-C:H layer

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We investigated the influence of a hydrogenated disordered carbon (*a*-C:H) layer on the nucleation of diamond. Substrates *c*-Si⟨100⟩, SiAlON, and highly oriented pyrolytic graphite {0001} were used in this study. The substrate surfaces were characterized with Auger electron spectroscopy (AES) while diamond growth was followed with Raman spectroscopy and scanning electron microscopy (SEM). It was found that on silicon and SiAlON substrates the presence of the *a*-C:H layer enabled diamond to grow readily without any polishing treatment. Moreover, more continuous diamond films could be grown when the substrate was polished with diamond powder prior to the deposition of the *a*-C:H layer. This important result suggests that the nucleation of diamond occurs readily on disordered carbon surfaces, and that the formation of this type of layer is indeed one step in the diamond nucleation mechanism. Altogether, the data refute the argument that silicon defects play a direct role in the nucleation process. Auger spectra revealed that for short deposition times and untreated silicon surfaces, the deposited layer corresponds to an amorphous carbon layer. In these cases, the subsequent diamond nucleation was found to be limited. However, when the diamond nucleation density was found to be high; i.e., after lengthy deposits of *a*-C:H or after diamond polishing, the Auger spectra suggested diamondlike carbon layers.

## I. INTRODUCTION

Although diamond has been shown to nucleate on a wide variety of materials,<sup>1-3</sup> the substrate's surface was, in most cases, treated to enhance nucleation density. Diamond powder and other types of abrasive polishing,<sup>4</sup> as well as ultrasonic polishing with a diamond powder suspension<sup>5,6</sup> have been shown to enhance nucleation density by several orders of magnitude. Two fundamentally different suggestions have been made to account for this effect.<sup>7</sup> It has been inferred from the nucleation and growth theory in metallic alloys that highly disordered surface material or microscopic defects in the polished surface could create sites that are preferred for the nucleation of diamond. On the other hand, residues (e.g., diamond fragments) from the polishing powder left adherent to, or imbedded in, the polished surface supply the nucleation sites for subsequent diamond growth.<sup>8,9</sup> Corroborating this latter assumption, Dubray *et al.*<sup>10</sup> related diamond nucleation enhancement to the presence of, what was identified as, amorphous carbon (*a*-C) left inside the scratches after diamond or graphite powder polishing.

Amorphous carbon layers can be modeled either as a random network of *sp*<sub>2</sub> and *sp*<sub>3</sub> bonds or as crystallites of graphite interlinked by an *sp*<sub>3</sub> bonded random network (see Ref. 11 for a review). One obvious suggestion should be that any *sp*<sub>3</sub> sites, or at least any cluster of *sp*<sub>3</sub> sites present on the surface of a carbon layer or revealed by atomic hydrogen etching during the early stages of diamond deposition, could

become a nucleation site for diamond crystallites. A large number of disordered carbon materials have been reported and their structural classification is not easy. Glassy and microcrystalline carbon are often related to graphite since they contain approximately 100% of *sp*<sub>2</sub> sites.<sup>11</sup> These materials are essentially metallic. Deposited *a*-C or *a*-C:H differ from glassy carbon in being truly amorphous and semiconducting.<sup>11</sup> Evaporated *a*-C films contain about 1%–10% of *sp*<sub>3</sub> sites, while *a*-C:H may comprise 30%–60% of hydrogen with perhaps 70% of *sp*<sub>3</sub> sites. Ion beam deposition methods are able to raise the proportion of *sp*<sub>3</sub> sites in both *a*-C and *a*-C:H films.

We report here an investigation of the influence on diamond nucleation of the deposition of an hydrogenated amorphous carbon (*a*-C:H) layer on the substrate surface. Substrates of *c*-Si ⟨100⟩, SiAlON and highly oriented pyrolytic graphite {0001} have been used in this study. SiAlON<sup>11-14</sup> is a solid solution of silicon oxynitride and alumina. The mechanical properties of this material make it a good candidate for cutting tools that work at high velocity and high temperature.

## II. EXPERIMENTAL DETAILS

The substrates were: silicon ⟨100⟩ from Virginia Semiconductors Inc., highly oriented pyrolytic graphite, and SiAlON from Kennametal, Inc. The surface preparation and coating procedures were as follows: (a) ultrasonic cleaning in acetone and deionized water, (b) ultrasonic

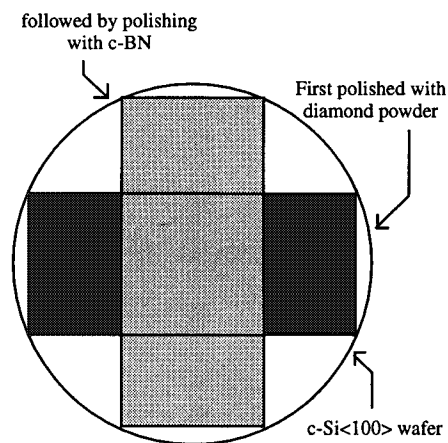


FIG. 1. Yarbrough's experiment (Refs. 7 and 10): the silicon wafer is polished with diamond powder in one direction, over a limited area. It is then polished with *c*-BN powder in a perpendicular direction. This enables us to have on the same sample areas that are: diamond and *c*-BN polished, diamond polished, *c*-BN polished, or unpolished.

cleaning in acetone and deionized water, followed by the deposition of an *a*-C:H layer, (c) diamond polishing, ultrasonic cleaning in acetone and deionized water, (d) diamond polishing, ultrasonic cleaning in acetone and deionized water followed by the deposition of an *a*-C:H layer. Polishing was carried out with 0.5  $\mu\text{m}$  diamond powder. One sample was prepared following Yarbrough's experiment<sup>7,10</sup> (Fig. 1) polishing with cubic boron nitride powder (0.5–1  $\mu\text{m}$ , Borazon, General Electric, Whorthington OH). Coatings of *a*-C:H were deposited in a dc plasma reactor using a 5% methane/hydrogen mixture at 50 mTorr and a low substrate temperature (100–200 °C). The estimated thickness ranged from 10 to 30 nm for deposition times varying from 5 to 15 min. The diamond films were deposited using a tubular microwave plasma reactor (Toshiba mod. TMG-132 F/U2). The microwave power source has a variable power in the range 0.1–1.5 kW and operates at a frequency of  $2450 \pm 20$  MHz. The substrate surface temperature was monitored with an optical pyrometer during the deposition. All the diamond films were deposited during 3 h using a 100 sccm gas flow of 1% of methane in hydrogen at a fixed pressure of 90 Torr. The temperature varied across the surface of the samples from 850 to 925 °C.

The number of nuclei as well as morphology of the films were investigated with a scanning electron microscope model ISI-SX-040. Raman spectra were measured on an ISA Jobin–Yvon Ramanor U-1000 spectrometer. Excitation was by means of the 514.5 nm line of an argon ion laser with an output power in the range of 100–500 mW. This instrument is equipped with a microprobe whose spot size is in the range of a few micrometers. AES measurements were carried out with a PHI spectrometer (CMA model 15-25G) set up for measurements in the first derivative mode with a 2  $V_{p-p}$  modulation voltage. The electron beam energy was 3 keV and the sample current was about 1  $\mu\text{A}$ . The pressure in the analysis chamber was in the range of  $6\text{--}8 \times 10^{-9}$  Torr.

### III. RESULTS AND DISCUSSION

#### A. Effects of surface treatments on diamond nucleation

The SEM photomicrographs of Fig. 2 indicate that the deposition of a 30 nm *a*-C:H layer yielded a good nucleation density ( $10^7/\text{cm}^2$ ) on silicon surfaces that were not polished, and a higher nucleation density on silicon surfaces that were first polished with diamond powder. Comparatively, unprocessed silicon wafers did not show any nucleation at all. The fact that one can achieve a high nucleation density after depositing an *a*-C:H layer on top of the diamond polished silicon surface is the main result of this paper. It leads to the important conclusion that the surface left after polishing with diamond powder does not have any intrinsic properties that enhance the nucleation such as defects in the silicon or the presence of diamond residue. It is the creation of a surface with disordered carbon that is critical, and its formation is indeed one step in the diamond nucleation mechanism.

Sample 4, referred to as Yarbrough's experiment, further confirms these conclusions. We observed on an equivalent sample that was not coated with an *a*-C:H layer,<sup>10</sup> that very few diamond crystals had nucleated on the *c*-BN polished area and that the diamond nucleation density was greatly reduced on the area that was polished with diamond and subsequently polished with *c*-BN powder. These results were compared to an area that was polished with diamond only. One can see on Fig. 3, that in the area that was polished with *c*-BN and subsequently covered with an *a*-C:H layer, the diamond nucleation density is high. More importantly, in the *c*-BN polished area, crystals do not follow the polishing direction and appear to be randomly distributed on the surface. In the area that was polished with both diamond and *c*-BN, the *a*-C:H layer has eliminated the preferential nucleation of diamond along diamond powder scratches.<sup>10</sup> This result indicates that the surface relief does not influence the reaction strongly. According to the size of the diamond crystals, all the nucleation events occurred approximately at the same time. It is therefore unlikely that, in the present case, delayed nucleation occurred in the *c*-BN polished area as Bachmann *et al.*<sup>15</sup> reported in their comparative study of the diamond nucleation efficiency of different abrasive powders. Similar results were found on the SiAlON substrates (Fig. 4) and further indicate that the disordered carbon plays an important role in the nucleation of diamond.<sup>16</sup>

Conversely, this nucleation enhancement due to *a*-C:H is not observed on graphite. This is demonstrated on Fig. 5. Some of our previous experiments on the same graphite substrates polished with diamond or boron nitride powder without any *a*-C:H overlayer lead to a continuous diamond film. In the present case, diamond crystals were only found in the form of clusters that vaguely followed the scratches left after polishing with diamond powder. This suggests that the structure of the carbon layer differs from the above experiments and was deposited more or less in the form of graphite, and not as an *a*-C:H layer, on the graphite substrate.

Figure 6 shows the Raman spectra of sample 2b, 3b, and 8b and demonstrates that the quality of the diamond was not altered by the presence of the *a*-C:H layer. Table I summar-

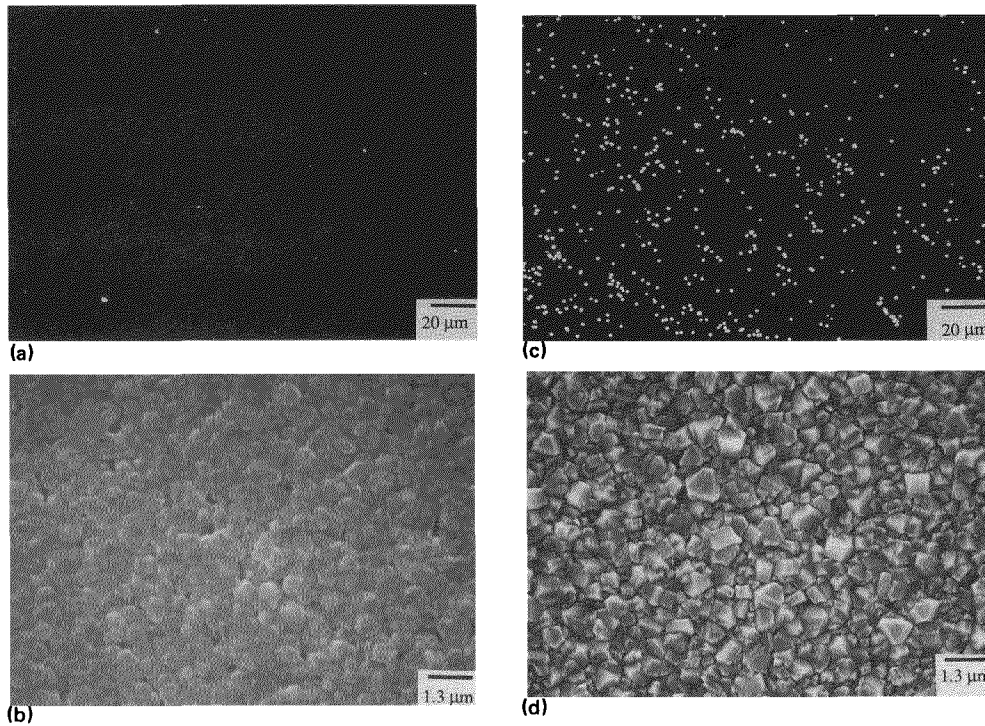


FIG. 2. SEM photomicrograph of diamond deposits after various surface preparation: (a,b) Si wafer on which an *a*-C:H layer had been deposited for 5 min, (c,d) Si wafer on which an *a*-C:H layer had been deposited for 15 min. (a,c) feature the sides of the samples that were not diamond polished, while (b,d) feature the sides that were polished (sample 2,3) prior to the *a*-C:H deposit.

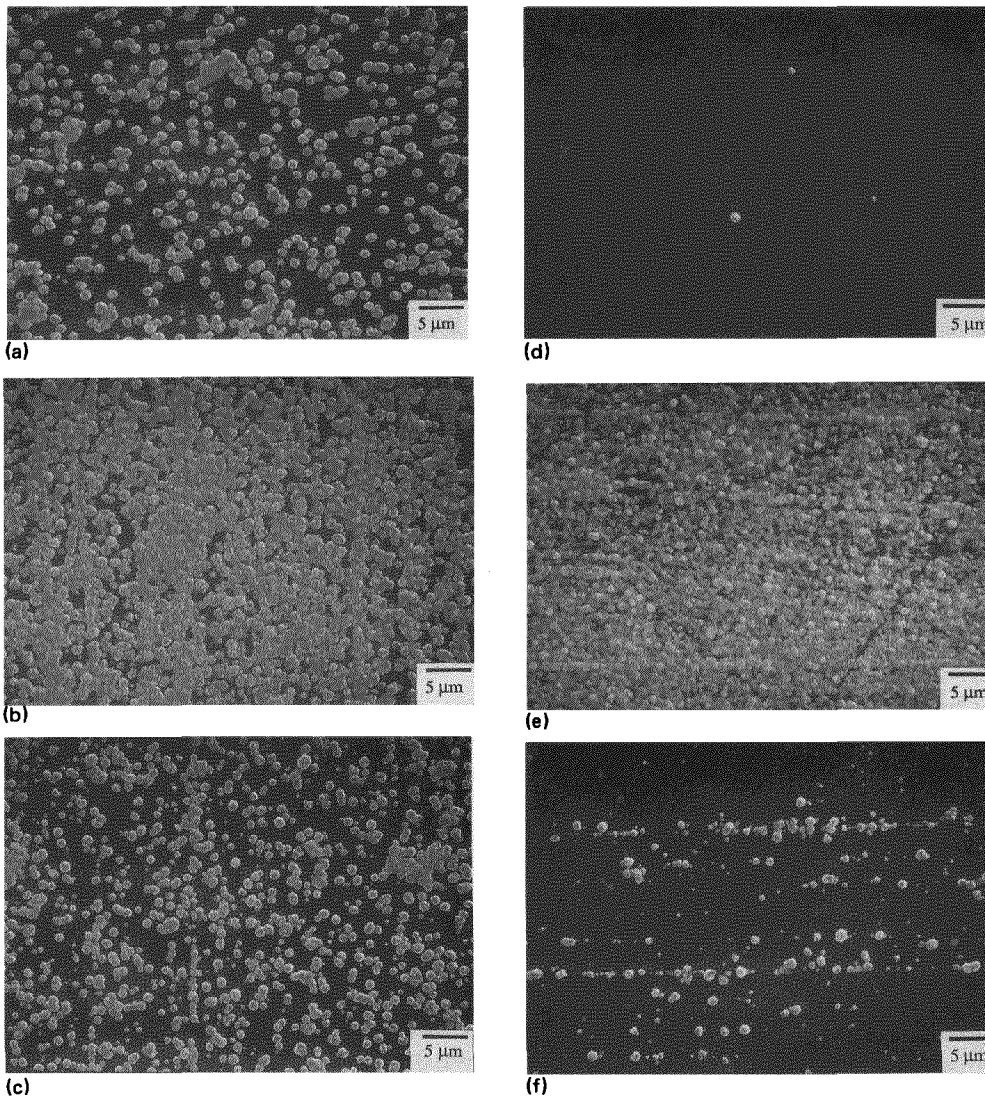


FIG. 3. SEM photomicrograph of sample 4 (referenced as Yarbrough's experiment): (a,b,c) Si wafer on which an *a*-C:H layer had been deposited for 15 min. Domains were respectively polished with *c*-BN (a), diamond (b) and diamond followed by *c*-BN (c). (d,e,f) same as the above, except that the substrate was not coated with an *a*-C:H film.

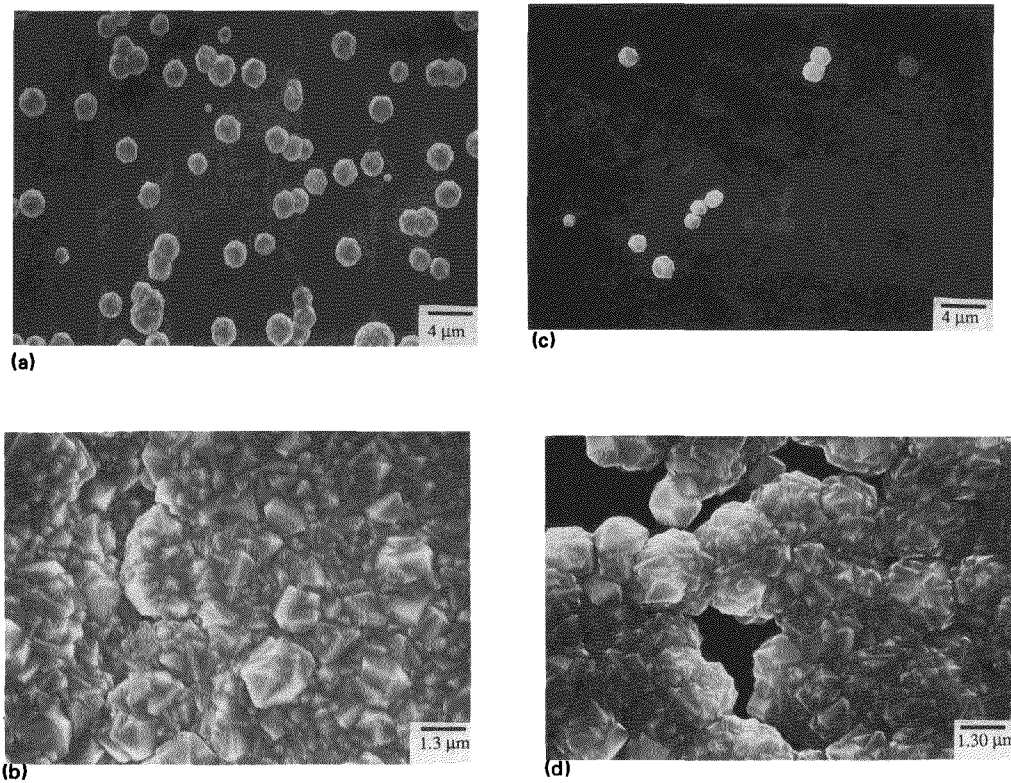


FIG. 4. SEM photomicrograph of diamond deposits: (a,b) SiAlON sample on which an *a*-C:H layer was first deposited for 5 min, (c,d) reference SiAlON sample without any *a*-C:H layer. (a,c) feature the sides of the samples that were not polished with diamond powder, while (b,d) feature the sides that were polished.

izes the diamond nucleation densities of all the samples. The diamond nucleation density tends to increase with the deposition time of the *a*-C:H layer. One can explain this result by considering that the number of nucleation centers imbedded

in the *a*-C:H layers increases with the layer thickness and consequently with the deposition time. Nucleation centers are then activated by etching processes during the first stages of the reaction. Neither the morphology, nor the size of the

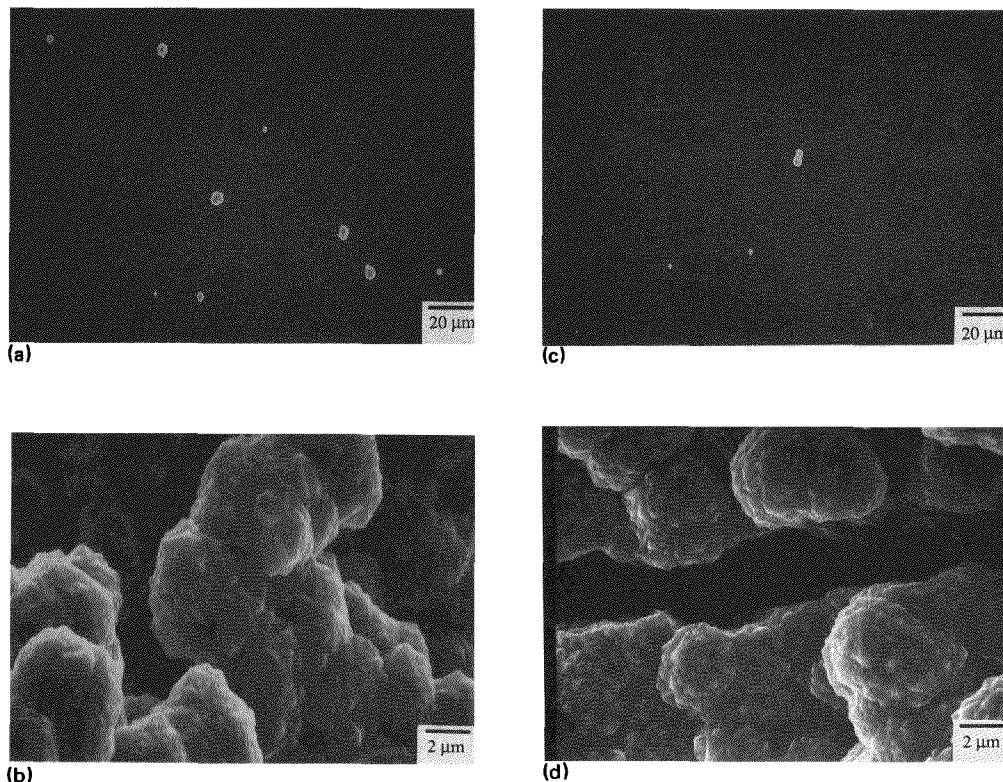


FIG. 5. SEM photomicrograph of diamond deposits: (a,b) graphite sample on which an *a*-C:H layer was deposited for 5 min, (c,d) reference graphite sample without any *a*-C:H layer. (a,c) feature the sides of the samples that were not polished with diamond powder, while (b,d) feature the sides that were polished.

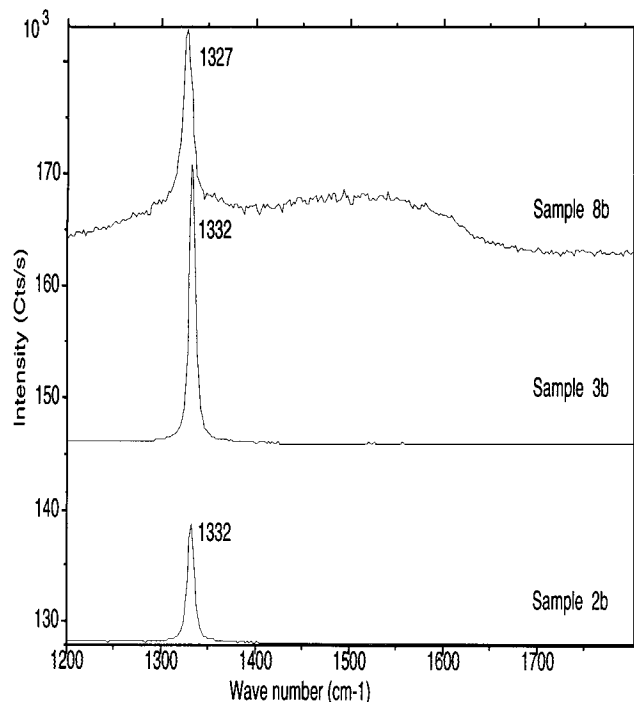


FIG. 6. Raman spectra of samples: (2b) *c*-Si substrate polished with diamond powder, on which an *a*-C:H layer was deposited for 5 min, and on which diamond was subsequently grown. (3b) *idem* as the above, but the *a*-C:H layer was deposited for 15 min. (8b) {0001} Graphite substrate, polished with diamond powder, on which an *a*-C:H layer was deposited for 5 min, and diamond was subsequently grown.

diamond crystals seem to be influenced by the presence of the *a*-C:H layer. The difference between the morphology of diamond crystals deposited on graphite samples and the ones deposited on silicon and SiAlON samples can be attrib-

uted to the local change in growth conditions induced by etching at the graphite surface. The high degree of renucleation exhibited by graphite samples is typical of high hydrocarbon concentrations, and it is believed that atomic hydrogen etching of the surface changes the hydrocarbon to hydrogen ratio. This phenomenon cannot be attributed to *a*-C:H deposits since it is observed on diamond polished graphite as well [Fig. 5(d)].

Although these first results indicate that *a*-C:H can be a precursor to diamond growth, they do not prove that diamond grows readily on amorphous carbon. The observations indicate that the formation of such a layer can be one step that leads to diamond nucleation. They are compatible with results found by Walrafen *et al.*,<sup>17</sup> who measured a succession of Raman spectra during diamond growth and found that diamond-like carbon can be found prior to diamond growth. In the second part of this section, we will investigate further the nature of the deposited *a*-C:H layer.

## B. Physico-chemical investigation of surface preparation

Several techniques can be used to determine the structure of a disordered carbon film (see Refs. 11 and 18 for a review). The bulk properties of the film can be investigated with nuclear magnetic resonance (NMR) or x-ray near edge structure (XANES),<sup>11</sup> whereas AES can be used to investigate the surface properties. Each allotropic form of carbon yields a different AES spectrum and while it is not always possible to determine the structural properties of a disordered carbon film such as the *sp*<sup>2</sup>/*sp*<sup>3</sup> ratio, it can be easily distinguished from any other stable or unstable form of carbon. Moreover, the volume probed by this surface analysis technique can be as low as a few nanometers in depth, and a few micrometers in diameter.

TABLE I. Diamond nucleation density as a function of substrate types and preparation conditions. In the *a*-C:H layer the *a*-C:H layer deposition time is indicated. Sample 4 was polished with both *c*-BN and diamond (see Sec. II), (BN) or (D) refer to an area that was polished only with *c*-BN or diamond, and (D&BN) refers to the area that was polished with diamond and subsequently polished with cubic boron nitride.

No.	Substrate	Polished	<i>a</i> -C:H	Density of nuclei
1a	Si	No	No	0
1b	Si	Yes	No	Continuous film
2a	Si	No	Yes (5 min)	$5-20 \times 10^4/\text{cm}^2$
2b	Si	Yes	Yes (5 min)	Continuous film
3a	Si	No	Yes (15 min)	$10^7/\text{cm}^2$
3b	Si	Yes	Yes (15 min)	Continuous film
4a	Si	Yes (BN)	Yes (5 min)	$3 \times 10^7/\text{cm}^2$
4b	Si	Yes (D)	Yes (5 min)	$10^8/\text{cm}^2$
4c	Si	Yes (D&BN)	Yes (5 min)	$5 \times 10^7/\text{cm}^2$
5a	SiAlON	No	No	$7 \times 10^5/\text{cm}^2$
5b	SiAlON	Yes	No	Continuous film
6a	SiAlON	No	Yes (5 min)	$5 \times 10^6/\text{cm}^2$
6b	SiAlON	Yes	Yes (5 min)	Continuous film
7a	Graphite	No	No	$4 \times 10^5/\text{cm}^2$
7b	Graphite	Yes	No	Continuous film
8a	Graphite	No	Yes (5 min)	$5 \times 10^4/\text{cm}^2$
8b	Graphite	Yes	Yes (5 min)	Large clusters of diamond crystals

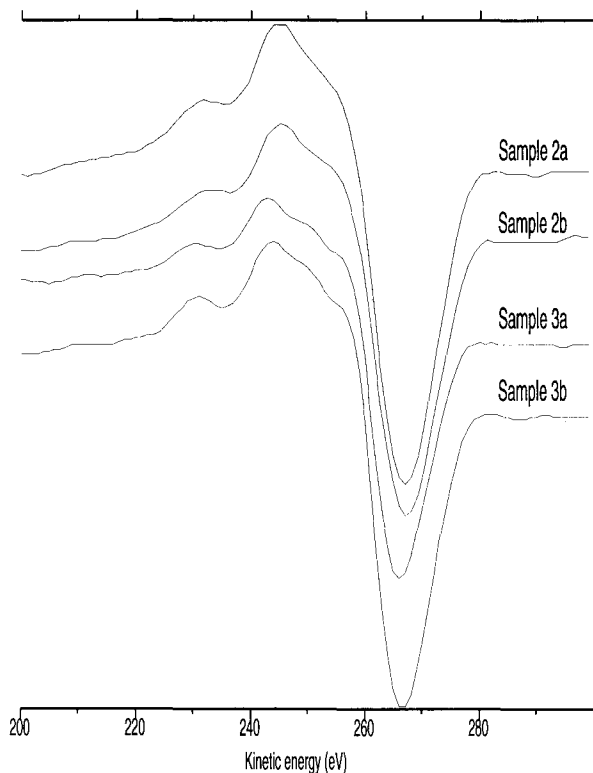


FIG. 7. Carbon *KLL* Auger spectra of samples: (2a) Unpolished *c*-Si substrate on which an *a*-C:H layer was deposited for 5 min. (2b) same as (2a), but the substrate was previously polished with diamond powder. (3a) and (3b) are respectively identical to (2a and 2b) but the *a*-C:H layer was deposited for 15 min.

Figure 7 presents the carbon *KLL* Auger spectra of samples 2a, 2b, 3a and 3b. The carbon layer thicknesses were estimated to range between 10 and 30 nm. The presence of silicon and oxygen in the spectra indicated nonuniform coatings in most cases. Nevertheless the carbon Auger lineshapes reveal that for short deposition times the deposited carbon is amorphous in type.<sup>19–21</sup> For longer deposition time, and for diamond polished surfaces, Auger spectra are similar to diamondlike carbon layers.<sup>22–24</sup>

Figure 8 presents the Auger intensities (normalized to 100%) measured along the surface of sample 2 and 3, revealing differences between the two areas (polished and unpolished). The carbon Auger signal increases in the region that was polished with diamond powder prior to the *a*-C:H deposition. This increase in intensity is believed to be due to the presence of disordered carbon left after diamond polishing,<sup>10</sup> on which the *a*-C:H layer simply piles up or deposits quicker. This small increase in carbon concentration yielded a much higher density of nuclei, which indicates that the structure of the layer is more important than its thickness.

#### IV. CONCLUSIONS

Altogether the results emphasize the role played by disordered carbon domains in the diamond nucleation process and leads to the following mechanism for explaining the effect of diamond polishing. They confirm that the role of diamond powder polishing could be to deposit a disordered carbon layer.<sup>10</sup> Once the sample is introduced into the reactor,

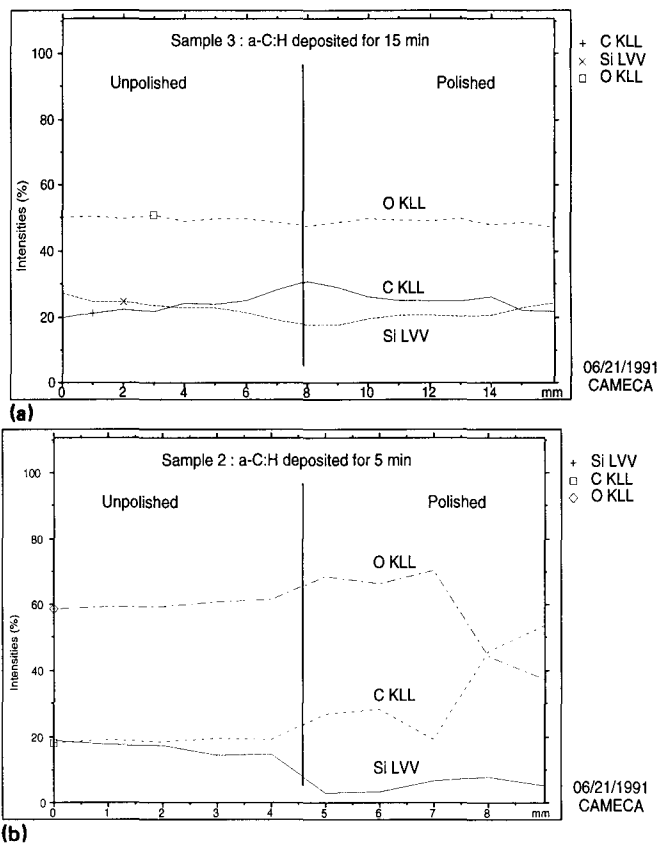


FIG. 8. Auger intensities (normalized to 100%, but not corrected from the sensitivity factors) measured on a scan along the surface's samples 2 and 3 (a) and (b), respectively).

atomic hydrogen, combined with the high temperature environment, will tend to etch this layer. Simultaneously, hydrocarbon species will start to deposit amorphous carbon, diamond-like carbon or diamond on the amorphous carbon layer left after polishing. This layer will also tend to react with the underlying silicon substrate to form silicon carbide which is believed to be amorphous.<sup>25</sup> Whenever the layer is thick enough to resist both the etching and the silicon carbide transformation, we propose, in agreement with many workers, that diamond crystals will be able to nucleate on the subjacent *sp*<sup>3</sup> bonded carbon (or on clusters of *sp*<sup>3</sup> bonded carbon) that comprise the diamondlike carbon layer. Therefore, the nucleation may be similar to diamond homoeptaxy. In the case where the initial disordered carbon layer is too thin or if its structure is such that it yields a high etching rate or a high silicon carbide conversion rate, it will be etched away or transformed before any nucleation event could occur. During diamond growth, both etching (if possible) and silicon carbide formation continue, and will eventually result in a diamond/silicon carbide interface. On clean unpolished silicon surfaces hydrocarbons will form carbidic bonds with silicon wherever amorphous carbon is not present.<sup>26,27</sup>

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