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Chemical Nucleation for CVD Diamond Growth

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Abstract: A new nucleation method to form diamond by chemically pretreating silicon (111) surfaces is reported. The nucleation consists of binding covalently 2,2-divinyladamantane molecules on the silicon substrate. Then low-pressure diamond growth was performed for 2 h via microwave plasma CVD in a tubular deposition system. The resulting diamond layers presented a good cristallinity and the Raman spectra showed a single very sharp peak at 1331 cm^{-1}, indicating high-quality diamonds.

Introduction

Nucleation and growth of heteroepitaxial diamond films represents one of the largest technological breakthroughs in materials science this century. Although no single-crystal thin films have up to date been deposed on nondiamond substrates, true heteroepitaxy remains as a goal for further research activities, due to the expected performance of such films in electronic applications.[1,2] Currently, diamond synthesis from chemical vapor deposition (CVD) is routinely achieved by more than 10 different methods. However, despite rapid progress, the growth on silicon substrate mediated by microwave plasma chemical vapor deposition (MPCVD) still needs a nucleation step, which is conventionally accomplished by a scratching pretreatment (diamond, oxides, silicides, nitride carbides, or borides) of the foreign support.[3] To avoid this deleterious surface pretreatment, Yugo and co-workers have developed an alternative nucleation method performed in situ during diamond CVD, which involves application of a negative direct current (dc) substrate bias.[4] More recently, Wolter and co-workers have reported a new process involving an alternating current (ac) bias source for bias-enhanced nucleation (BEN) to produce highly oriented diamond (HOD) on Si(100).[2,5] Finally, some procedures require thin metal films, graphite fibers, fullerenes, amorphous carbon films, implanted C+ films, or mineral oil, for example, as a precursor.[6] The ability of structured organic surfaces to control nucleation of crystal growth in biological and synthetic environments[7−14] has prompted a number of model studies on oriented crystallization of inorganic and organic materials using Langmuir monolayers,[15−19] biological macromolecules,[9,20] and functionalized polymer surfaces.[21−23] Although these organic surfaces are able to induce oriented growth of crystals, the specificity of face-selective nucleation has generally not been high, and the processes could not be easily controlled because the structures of these organic surfaces were neither homogeneous nor well-defined. Only a limited number of substrates are available to which current monolayers can be attached in a simple manner. Organosulfur adsorbates,[24] for example, are only suitable for use with non-oxide transition metal surfaces:

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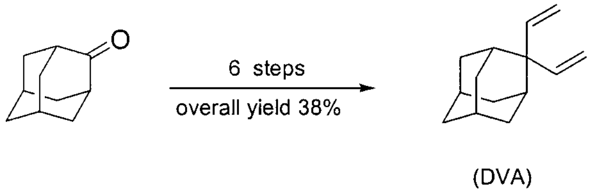
Scheme 1. Synthesis of the 2,2-Divinyladamantane (DVA) in 6 steps starting from 2-adamantanone



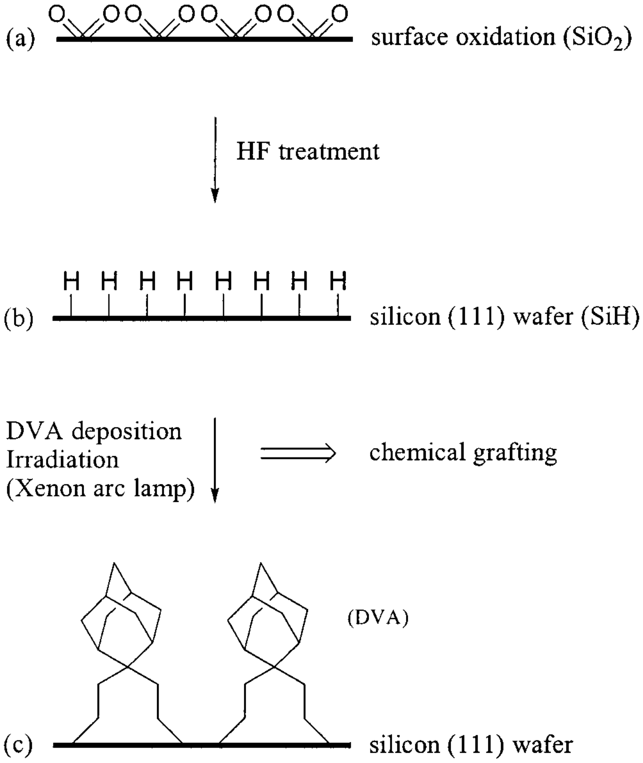
formation of organosulfur SAMs on gold surfaces[25] is partially facilitated by the absence of a native oxide layer on the gold surface, which is an otherwise uncommon feature of many metals. Sato[26] and Olah[27] suggested that hydrocarbon cage molecules such as adamantane could be possible embryos for diamond nuclei formation in the gas phase.

Linford and Chidsey[28] have recently described the first example of a densely packed stable organic monolayer covalently bonded directly to the silicon surface. A combination of these findings led us to the design of an adamantane derivative capable of being covalently attached 2-fold to the silicon surface. Molecular modeling revealed a chain length of two carbon atoms for fixing an adamantane molecule via two tethers to two adjacent silicon atoms of a (111) surface with minimal steric strain. The results of this information converged to the 2,2-divinyladamantane (DVA) as the target molecule to be attached via double hydrosilylation (see Scheme 2). In this paper we report the study of a new process[29] to obtain diamond nucleation on a silicon surface via chemical pretreatment, which involves covalently bonded organic molecules on the silicon substrate.

Results and Discussion

Consequently, starting from 2-adamantanone, we synthesized in 6 steps and 38% overall yield this new derivative of adamantane (DVA)[30] containing two alkene chains, with the aim of using it as a seed for the nucleation and growth of diamond on a (111) silicon surface (Scheme 1). Grafting of the DVA molecules to the silicon (111) surface was carried out next. In our ongoing exploration of effective methods to prepare adamantane derivatives capable of being covalently attached to the silicon surface, we showed that 2,2-divinyladamantane reacts with different bis(hydrosilanes) to give selectively disilacyclic compounds in high yields.[31] The observed competition between the intra- and intermolecular processes, leading to disilacyclic compounds and oligomers, respectively, illustrates the critical importance of the bis(hydrosilane) geometry for the selectivity. Among numerous known techniques of hydrosilylation reactions, i.e., transition metal complex catalysis,[32] free-radical conditions,[33] and initiation by ultraviolet light or organic peroxides, we have chosen the photochemical process,[34] which ensures a minimal contamination of the silicon surface by chemical products.

Scheme 2



From undoped silicon (111) wafers, 10 × 10 mm^2 squares were cut. Prior to the deposition, they were consecutively washed with deionized (DI) water, immersed for 30 min in aqueous hydrofluoric acid (Fluka, HF > 40%) to remove any existing native oxide (Scheme 2a) and to create a hydrogen-terminated silicon surface with a defect density of 5×10^{-3} cm^{-2},[35] thus exposing the hydrogen atoms perpendicular to the Si surface (see Scheme 2b), rinsed in DI water, blown dry with nitrogen, and finally dried during 3 h under the vacuum of a turbomolecular pump (Scheme 2b). This procedure was shown to be the best one to obtain minimal surface oxidation and hydrocarbon contamination of the samples, which prevent the chemical reaction of DVA grafting on the silicon surface. Indeed, the Si−C bond between DVA molecules and silicium atoms is formed after homolysis of a Si−H bond by UV treatment, and reaction of the resulting silyl radical on the DVA vinyl groups.

The binding of the DVA on the surface was performed as follows. The silicon squares were placed into a glass balloon under a nitrogen atmosphere and a drop of DVA was deposited on their surface. To avoid reoxidation of the silicon surface during the chemical reaction, the balloon was then rapidly evacuated to ∼1 mbar with an oil rotary pump and flooded with

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nitrogen, and the sample was irradiated with a Xenon arc lamp (OSRAM XBO 450 W) using a liquid light guide (cut off ≤280 nm) to avoid heating the reaction mixture, for ~24 h. Under the applied wavelength, homolysis of the Si−H bond occurred, initiating the bis-hydrosilylation process that allowed formation of the disilacyclic compound after covalent bonding between DVA and silicium atoms (Scheme 2c). The wafer was then rinsed repeatedly with ethanol and DI water to eliminate the excess of DVA and physisorbed material and sonicated twice for 5 min each time in fresh portions of dichloromethane (CH_2Cl_2) to remove ungrafted DVA molecules, and traces of solvents (ethanol and dichloromethane), which are susceptible to initiate nucleation, were completely removed by drying the samples under high vacuum (5 10^{-6} mbar) for 12 h prior to further characterization studies.

After the chemical grafting, each sample was analyzed by X-ray photoelectron spectroscopy (XPS: VG ESCALAB V spectrometer equipped with a MgKa 1253.6 eV and a SiKa 1740 eV twin anode) to observe the species present on the surface and placed into the MPCVD chamber[36] for the diamond growth treatment.[37] The growth rate is a function of the time and varies from less than 1 μm/h to 1 mm/h according to the deposition technique.[38−41] Without prior etching with H_2, the deposition (120 min) was performed in a 1% CH_4:H_2 gas mixture at a pressure of 40 mbar[42] and a temperature of 850 °C.[43] At the end a 5 min post-treatment was applied in pure hydrogen plasma at the same pressure and temperature to remove the remaining non-diamond phases.[44] Finally, the samples were characterized by XPS and Scanning Electron Microscopy (SEM: ZEISS GEMINI electron microscope).[45]

Five different samples were prepared and treated as summarized in Table 1. This series was intended to evaluate the contribution of each step of the treatment on the development of diamond nuclei.

Table 1. Pretreatment Performed on Silicon (111) Surfaces before Diamond Growth

sample	HF cleaning	DVA drop	UV treatment	CVD diamond growth
1	no	no	no	yes
2	yes	no	no	yes
3	yes	no	yes	yes
4	yes	yes	no	yes
5	yes	yes	yes	yes

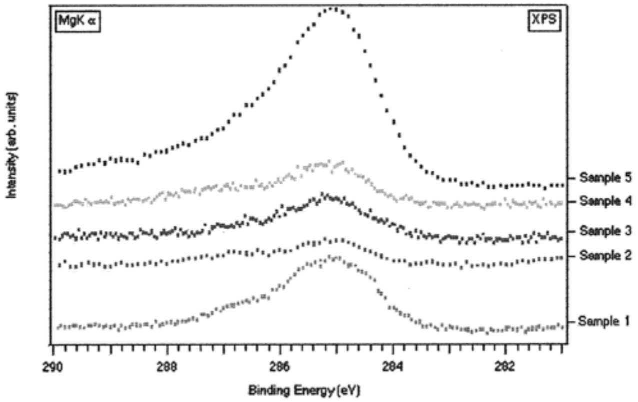

Figure 1. XPS analysis of differently pretreated samples (cf. Table 1): carbon 1s peak progressions.

Each sample was submitted to XPS studies, which allows measure of the carbon 1s core-level signal considered as an indicator for the quantity of carbon attached to the surface (Figure 1). In fact, only sample 5, which had received the full treatment, i.e. HF cleaning, DVA deposition, and UV irradiation, showed an intense C 1s signal (285 eV) assigned to C−C bonding, suggesting that DVA covered the silicon surface. Deconvolution of the C 1s signal revealed 2 peaks: the biggest, of approximately 99.6% present at 285.2 eV, is characteristic of C−C bonding and the smallest, of approximately 0.4% at 283.7 eV, is characteristic of C−Si bonding.[46] Samples 2 to 4 presented a constant very low intensity for the signal corresponding to C 1s (285 eV) independently of the previous treatment. The weak signal observed for sample 1 was attributed to the amount of carbon contaminating the silicon (111) wafer, remaining in the absence of HF cleaning. This result corresponds to those observed previously by other researchers.[47]

The following experiment was performed to confirm the covalent attachment of DVA on the silicon surface. The geometric configuration of the ensemble photon-source/sample/electron-detection was varied at incident angles of 90°, 30°, and 10° between the sample and the electron detector (Figure 2). The C 1s signal was analyzed and each peak contribution was assigned after deconvolution. Thus, we observed that the C−Si peak at 283.7 eV increases (0.4% to 78.6%) and the C−C peak at 285.2 eV decreases (99.6% to 21.4%) when the incidence angle decreases (90° to 10°) (Table 2). This variation of the C−Si peak with the incidence angle proves that the DVA molecule is covalently bonded to the silicon surface.

The five samples were entered into the growth chamber and deposition was performed under the conditions described above, for 2 h. The plasma was then turned off, the chamber was pumped down, and the samples were transferred into the analytical chamber. A scanning electron microscope (SEM) inspection of the surfaces of pretreated samples 1 to 4 revealed

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(36) The deposition system used here is a self-made microwave plasma tubular reactor system. It consists of a 4 cm outer diameter silica tube that runs through bores in a rectangular metal microwave guide from Muegge (MW-GIRYJ 1540-1K2-08, 2.45 GHz, 1.2 kW). Irradiating the low-pressure inside the reactor tube with a microwave (480 W) ignites a plasma discharge. Kamo, M.; Sato, Y.; Matsumoto, S.; Sekata, N. *J. Cryst. Growth* **1983**, *62*, 642.

(37) The roughness variation of the grown diamond film is measured in situ by reflection of a He−Ne laser radiation (632.8 nm) on the surface of the substrate. The incident beam is modulated at 20 Hz (chopper) and the reflected signal is read synchronously through a lock-in amplifier (Brookdeal) to avoid noise signals from ambient light.

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(42) The hydrogen (Carbagas, purity 6.0) and the methane (Carbagas, purity 4.5) gas flows are regulated by MKS flow meters. A Leybold-Heraeus turbopump (Turbotronik NT 20) ensures a base pressure of 10^{-6} mbar while, during the deposition, pumping by a rough pump (Alcatel 10 m^3/h) through a needle valve is sufficient to get a pressure of 20 to 40 mbar in the tubular reactor. The pressure is measured by a cold cathode gauge control from 10^{-9} to 10^{-3} mbar by a Pyrani−Penning manometer from 10^{-3} to 1 mbar and by a piezoresistive pressure gauge (Haenni) from 1 to 100 mbar.

(43) The substrate temperature is optically measured by an Ircon Mirage pyrometer (single wavelength) from above the substrate and is stabilized by plasma heating through slight modification of the incident microwave power (~24 W) and additionnal cooling by air flux around the silica tube.

(44) The substrate position relative to the plasma discharge is modified by pulling up or down the microwave guide. The deposition system is computer controlled (Macintosh IIx) to allow perfect reproducibility. A LabView (National Instruments Corporation) routine controls the system through a 2308 I/O Black*Star interface.

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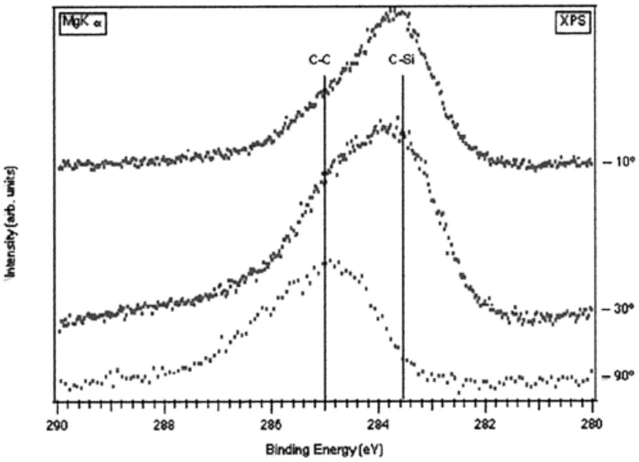

Figure 2. XPS analysis of sample 5 as a function of the collection angles: contributions at 283.7 and 285.2 eV are assigned to C−Si and C−C bonds, respectively.

Table 2. Quantification of Species on the Surface of Sample 5 at Various Collection Angles As Calculated from XPS Peak−Area Ratios and Relative Sensitivity Factors

	carbon 1s peak ratios	
angle (deg)	*I* C−C	*I* C−Si
90	99.6%	0.4%
30	37.1%	62.9%
10	21.4%	78.6%

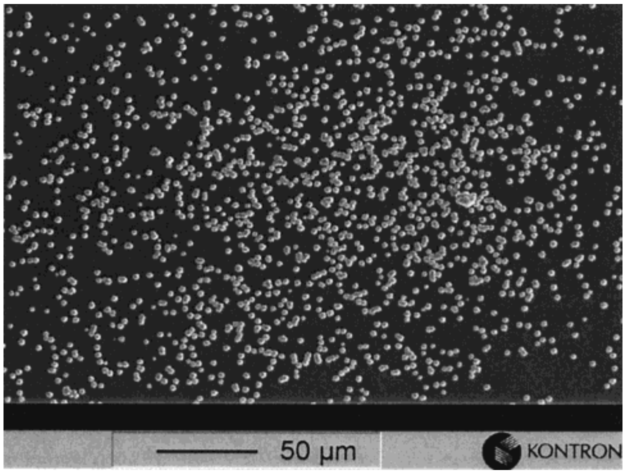

Figure 3. SEM micrograph of sample 5 after 2 h of CVD.

only a few diamond grains and a nucleation density below ~10^4 cm^{-2}. On the SEM image of sample 5, which received the full treatment, nucleation density rises to 10^9 cm^{-2} with a very homogeneous diamond size of about 2 μm (Figure 3). Those values are on the order of the ones obtained after nucleation by biasing (10^8−10^{11} cm^{-2}),[48] which constitutes the best actually known technique in this field.

Although the photochemical treatment is expected to densely cover the surface with covalently bound adamantane, the subsequent CVD plasma conditions will remove all the singly and presumably a few doubly attached molecules. The fact that nucleated diamonds were effectively obtained in sample 5 shows the stability of grafted DVA in the nucleation conditions. Indeed, all the samples treated without preliminary UV DVA grafting suffered no nucleation. This nucleation method therefore offers on top of the advantage of flexibility and mildness,[49] the possibility of photolithographic nucleation: diamonds adopt a homogeneous spatial repartition in the center of the irradiated region, with a well-facetted shape due to their cubic structure, while nucleation density sharply decreases to ~5 × 10^6 cm^{-2} on the brink of the irradiated region without even using a light mask.

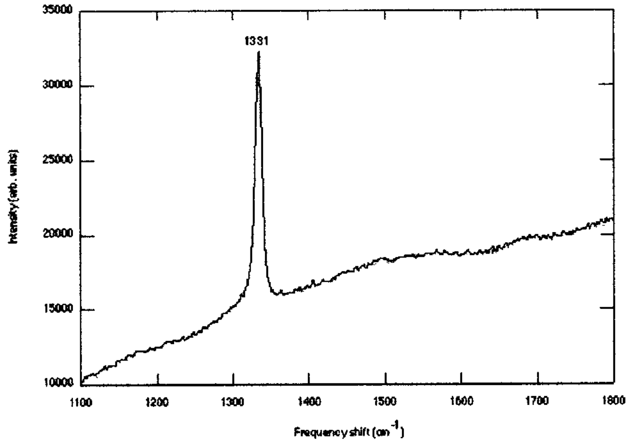

Figure 4. Raman spectrum of a diamond crystal on sample 5 after 2 h of CVD.

The Raman spectrum of sample 5, recorded with a multichannel DILOR XY instrument equipped with an optical microscope, is displayed in Figure 4. Measurements on individual crystals exhibited only the specific line centered around 1331 cm^{-1}. The sharp diamond peak and the absence of graphitic peaks near 1580 cm^{-1} reinforce the expectation, after prolonged CVD treatment, of diamond films with a high nucleation density and a large number of grain boundaries.[50] Despite the absence of a continuous diamond film after 2 h of treatment, outlining the still insufficient nucleation density, the presence of fixed and oriented DVA molecules bonded to the silicon surface should initiate a directed diamond growth, leading to the formation of oriented diamond films. Moreover, utilization of a laser beam instead of a Xenon arc lamp should increase the DVA grafting density.

Conclusion

We have presented a photochemical process for binding covalently an adamantane derivative (2,2-divinyladamantane, DVA) on a silicon substrate that may be used as an effective means of nucleation enhancement. The presence of the adamantane derivative and UV light were found indispensable in promoting an efficient nucleation (increasing the nucleation density by over 5 orders of magnitude). Surface analysis as well as high-resolution XPS, SEM, and Raman spectroscopy were used to study the nucleation and growth of diamond. The advantage of the method is its great flexibility: a possible application, i.e., production of patterned diamond films with the help of UV laser beams to draw on the silicon surface, is presently being studied.

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