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LABORATORY INVESTIGATION OF HYDROGENATED DIAMOND SURFACES: IMPLICATIONS FOR THE FORMATION AND SIZE OF INTERSTELLAR NANODIAMONDS

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ABSTRACT

The formation and size of interstellar diamonds have been investigated by infrared spectroscopy in the laboratory. Employing hot-filament chemical vapor deposition (CVD) to synthesize the interstellar analogs, we successfully reproduced the infrared emission bands of nanodiamonds around HD 97048 and Elias 1. Analysis of the infrared absorption spectra of synthetic diamond crystallites (25–700 nm) from a commercial source reveals a strong size-dependent effect. The 3.53 μm feature emerges only for particles larger than 25 nm. Our experiments suggest that the carriers of the anomalous infrared emission bands at 3.43 and 3.53 μm could be nanodiamonds that are larger than 25 nm and are formed by a CVD-like process.

Subject headings: infrared: ISM — ISM: individual (Elias 1, HD 97048) — ISM: lines and bands — ISM: molecules — methods: laboratory

1. INTRODUCTION

The existence of diamonds in space has been an interesting subject in the astrophysical community over decades. The material was first proposed as a component of interstellar dust to account for the ultraviolet extinction in the diffuse interstellar medium (Saslaw & Gaustad 1969). Its presence was later established after identification of presolar nanometer-sized diamond grains in primitive carbonaceous meteorites (Lewis et al. 1987). Recently, direct evidence for the existence of diamonds or diamond-like materials in interstellar space was provided by Guillois, Ledoux, & Reynaud (1999), who pointed out a close resemblance of the infrared emission bands observed for Elias 1 and HD 97048 (Geballe 1997; Van Kerckhoven, Tielens, & Waelkens 1999) to the CH stretch absorption bands of hydrogen-terminated surfaces of diamond nanocrystallites studied in our laboratory (Chang et al. 1995).

The identification of diamonds in space, in addition to the discovery in meteorites, supports the idea that interstellar diamonds could be formed through a chemical vapor deposition (CVD) process (Hecht 1987; Lewis et al. 1987; Nuth 1987; Wdowiak 1987; Daulton et al. 1996). For the diamonds around HD 97048 and Elias 1, Guillois et al. (1999) argued that because of the close proximity to these two young stellar objects, the grains are exposed to strong UV fluxes and can reach high temperatures (up to 1000 K). These conditions are reminiscent of the plasma conditions used in CVD diamond synthesis (Spear & Dismukes 1994). This CVD-like mechanism has been tested, and the possibility of having hydrogenated amorphous carbon as the diamond growth precursor has been examined by Duley & Grishko (2001). However, up to now, we know of no experiment that was able to reproduce the astronomical spectra with diamond films produced by CVD in laboratory. In § 2 of this Letter, we present the results of our efforts to simulate the interstellar diamond formation through a CVD process with the use of only H_2 and CH_4 as the precursors, followed by intensive hydrogen etching of the diamond films to reproduce the “anomalous” infrared emission features (Schutte et al. 1990).

Section 3 of this Letter is focused on the size of the diamond particles around HD 97048 and Elias 1. In primitive meteorites, diamonds are more abundant than other presolar grains by over 2 orders of magnitude, but their sizes are very small, about only 1–3 nm in diameter (Daulton et al. 1996). They have been expected to be the sizes of the carriers of the anomalous infrared emission bands. Van Kerckhoven, Tielens, & Waelkens (2002) recently suggested that the sizes of these carriers should fall between 1 and 10 nm, arguing that the surfaces of smaller (<1 nm) and larger (>10 nm) particles can be easily graphitized by stochastic and radiative heating. The suggestion, however, is at variance with our laboratory observations for detonation-synthesized 5 nm diamonds (Chen et al. 2002) and Orgueil meteoritic nanodiamonds, both of which do not show the characteristic 3.43 and 3.53 μm features. Caution should thus be exercised for the size analysis. In this work, we carry out further size analysis of diamond particles from 700 nm down to 25 nm in an attempt to understand fully how the observed spectra are correlated with particle size.

2. SIMULATION OF DIAMOND FORMATION

Standard hot-filament chemical vapor deposition (HFCVD) was brought about to synthesize the interstellar diamond analogs. The diamond film was deposited on a single-crystal silicon wafer using H and CH_x ($x = 1$–3) generated by tungsten hot filaments. The Si(100) substrate was first sonicated in diamond abrasive slurry for several hours to increase surface roughness and, hence, the diamond nucleation sites. The substrate was then horizontally mounted on a Mo plate with a distance of 11 mm from a 10 cm long, 10-coiled tungsten filament. A gas mixture of CH_4/H_2 (1/99 volume %) was introduced through a stainless steel nozzle with a distance of 13 mm from the filament. Diamond deposition was performed continuously for 12 hours with a filament temperature of 2500 K, a substrate temperature of 1150 K, a steady-state pressure of 30 torr, and a gas flow rate of 200 standard cubic centimeters per minute (sccm).

Raman spectroscopy of the as-deposited film confirmed the existence of sp^3 carbon atoms from the characteristic diamond peak at 1332 cm^{-1}. Scanning electron microscopy revealed that the as-grown particles have a typical size of several microns (Kweon, Lee, & Kim 1991). For the infrared spectroscopic measurements, the diamond film was transferred to a Ta sample holder positioned in a small high-vacuum chamber (Lin et al.

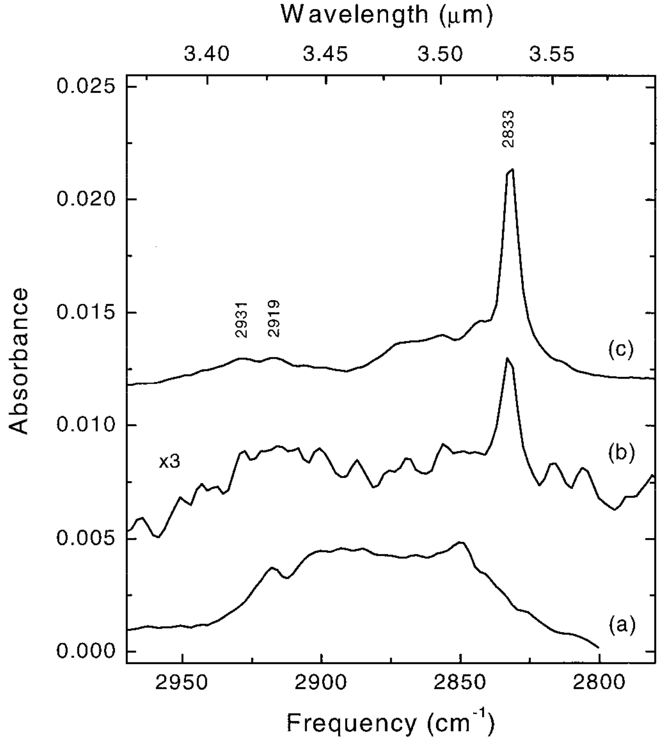

FIG. 1.—Infrared absorption spectra of an as-deposited HFCVD diamond film (*a*) before and (*b*) after etching with atomic hydrogen generated by hot filaments, followed by (*c*) oxidation at 900 K and rehydrogenation of the diamond surfaces at 1200 K. The oxidation, preferentially etching away graphitic carbons and thus increasing the exposed surface area of sp^3 carbons, effectively enhances the signals by a factor of ~10. The peak position of the most prominent feature stays the same at 2833 cm^{-1} in (*c*).

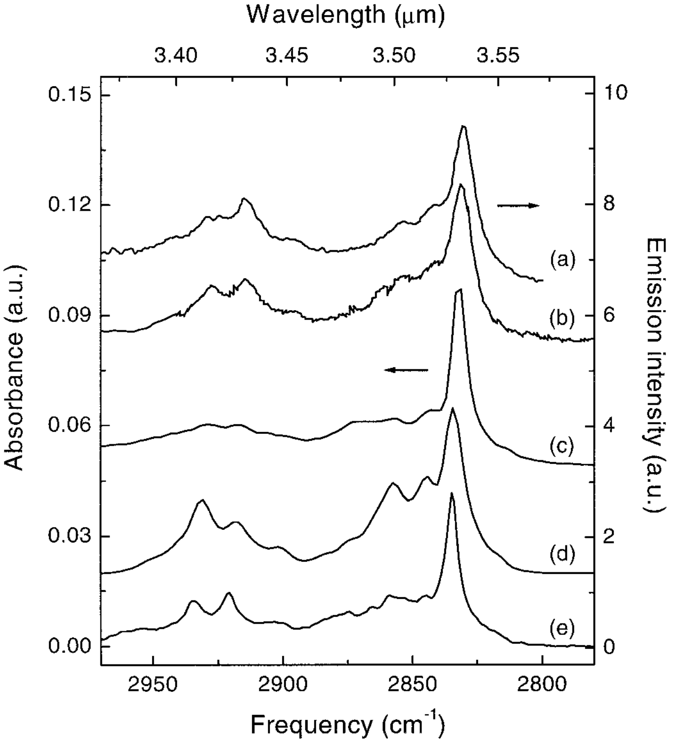

FIG. 2.—Comparison of infrared *emission* spectra of (*a*) Elias 1 and (*b*) HD 97048 with infrared absorption spectra (*c*–*e*) of synthetic diamonds observed in our laboratory. The absorption spectra were acquired for two different samples H-etched using two different methods: (*c*) CVD-synthesized particles and hot-filament plasmas, (*d*) 100 nm particles and hot-filament plasmas, and (*e*) 100 nm particles and microwave plasmas. All the absorption spectra are taken at room temperature.

1996). The film was first annealed to 900 K (30 minutes) under vacuum for thorough baking and degassing. The step serves to minimize spurious CH backgrounds resulting from contamination with organic compounds in ambient air. A Fourier-transform infrared spectrometer (Bomem MB154, Canada) acquired the infrared spectra following each treatment without removing the sample from the chamber. Analogous to scans conducted in single-crystal experiments (Cheng et al. 1997a; Cheng, Lin, & Chang 1997b), reference scans were taken after in situ oxidation of the diamond surfaces with 10 torr of pure O_2 at 900 K for 30 minutes to eliminate surface-bonded H. All the spectra are acquired after 400 scans with an instrumental resolution of 4 cm^{-1} at room temperature.

Prior to hydrogenation/etching treatments, broad absorption bands of CH stretches are observed between 2800 and 3000 cm^{-1} (or 3.33–3.57 μm) for the as-deposited film (Fig. 1*a*). The spectrum is typical for diamond films (Dischler et al. 1993; John et al. 1993), having poorly defined crystal surfaces and with graphitic structures inevitably formed in the CVD process. However, upon exposure of the as-deposited film to atomic H produced by cracking pure H_2 (20 torr, 200 sccm, and 30 minutes) at a substrate temperature of 1200 K, the spectrum is greatly simplified. A weak but characteristic transition emerges at 2833 cm^{-1}, as shown in Figure 1*b*. To further increase the signals, in situ oxidation of the film with pure O_2 (10 torr, 200 sccm, and 90 minutes) was performed to remove graphitic carbons. The CH stretching modes on C(111), C(110), and C(100) surfaces all appear after the oxidation and subsequent rehydrogenation (Fig. 1*c*). To this end, the infrared absorption spectrum that closely matches the astronomical emission spectra is obtained in the laboratory (Figs. 2*a*–2*c*).

The profound effect of H treatment on the spectral change, as seen in Figures 1*a* and 1*b*, has been understood as a result of the unique H-etching anisotropy on diamond surfaces (Cheng et al. 1997a; Hong & Chou 1998). Our previous investigations of diamond single-crystal surfaces by using both infrared spectroscopy and low-energy electron diffraction demonstrated that in the presence of H, 111-oriented facets are irreversibly formed on both C(110) and C(100), whereas C(111) remains as a stable surface at a substrate temperature of 1100 K (Cheng et al. 1997a). Such a dramatic crystal orientation dependent effect is observed only for diamond but not for silicon, and it is this exceptional property of diamonds that has made spectroscopic identification of interstellar nanodiamonds possible. We assign the observed absorption feature at 2833 cm^{-1} to the stretch of CH on well-defined C(111)-(1 × 1) facets and the weak doublet at 2919 and 2932 cm^{-1} to the CH stretches on the C(100)-(2 × 1) surface (Cheng et al. 1996; Lin et al. 1996).

3. SIZE ANALYSIS OF INTERSTELLAR NANODIAMONDS

Careful size analysis was carried out making use of diamond's unique surface properties. As suggested by Lewis, Anders, & Draine (1989), oxidized nanodiamonds may be terminated with weakly acidic groups. They can form negatively charged colloids at high pH (dispersed by charge repulsion) and tend to coagulate at lower pH (attracted by van der Waals forces). By adjusting the pH, nanodiamonds can be either dispersed or aggregated for size selection or recollection. We started the separation with 6 g of 100 nm synthetic diamonds (the smallest size available from Kay Industrial Diamond Corporation, USA), cleaned and oxidized by hot acid mixtures (Mitsuda et al. 1991), and dispersed in 0.1 M NH_3 (Hill et al. 1997). The milky, slurry-like diamond suspension sequentially went through membrane filters (Millipore, USA) with average pore sizes of 50 and 25 nm. The precipitants and the final superemnant were then collected and acidified by droplets of $HCl_{(aq)}$. Flocculation occurred within 2 minutes, and the solution was warmed overnight to ensure complete coagulation. Centrifugation (3 hr × 1000 g) followed to collect the flocculants. The precipitants were finally removed, deposited on a Si(100) wafer, and dried in a hydrocarbon-free desiccator to form a thin film (Chang et al. 1995). Typically 3 mg of the smaller particles (25–50 nm and <25 nm) was obtained in each extraction. Nanodiamonds of a size of 700 nm from the same source were also treated with the same procedures except that they have not gone through any filtration steps.

Comparison of the infrared absorption spectra of particles with different sizes shows a correlation between the absorption intensity of the 2835 cm^{-1} band and the particle size. In Figures 3*a* and 3*b*, the general features of the spectra of both 700 and 100 nm diamonds appear quite similar to those of the HFCVD film (Fig. 2*c*). The stretching mode of the tertiary CH on C(111)–1 × 1 still dominates the spectrum, while there are more shoulders present in the higher frequency side. A transition takes place as the particle size decreases. At a size in the range of 25–50 nm (Fig. 3*c*), the characteristic CH absorption at 2835 cm^{-1} diminishes to only a shoulder. Down to particles smaller than 25 nm (Fig. 3*d*), the tertiary CH peaks disappear nearly completely, and the absorption bands of CH_x on various facets merge into two unresolved envelopes. This spectral evolution, particularly the 2835 cm^{-1} band, clearly demonstrates that the CH stretching spectra can reflect the size of the nanodiamonds in the range of 10–100 nm.

Intuitively, one anticipates that the surface of such small nanodiamonds (<25 nm) should be ill defined, with steps breaking the surfaces into even smaller domains. Since the CH stretching features of hydrogenated diamond surfaces have been shown to depend strongly on surface morphology (Cheng et al. 1997a), one should not be too surprised that such surface vibrational modes can be sensitive probes to particle size. The reason that the characteristic absorption band at 2835 cm^{-1} is not seen for particles smaller than 25 nm is because H-etching is incapable of creating (111) domains that are large enough to yield the CH absorption features as those given by single crystals (Chen et al. 2002). It is of interest to note that two similarly broad bands have been observed for SiH stretches at ~5 μm on H-passivated silicon nanoparticles with sizes smaller than 10 nm (Schuppler et al. 1995).

Comparison of the astronomical spectra in Figures 2*a* and 2*b* with those in Figure 3 leads us to the suggestion that diamond grains larger than 25 nm exist in interstellar space. This suggestion, however, does not preclude the existence of smaller interstellar nanodiamonds. Indeed, the astronomical spectra are very possible to be a superposition of nanodiamonds of different sizes. It is generally believed that small diamond particles are much more abundant in space, according to the findings in meteorites and the analysis of the size distribution of nanodiamonds resulting from a condensation process (Anders & Zinner 1993; Daulton et al. 1996). Unfortunately, in our experiment, diamond particles smaller than 25 nm cannot be unambiguously identified because of the lack of characteristic features in the region of CH stretches as well as in the lower frequency regimes (Ando et al. 1993).

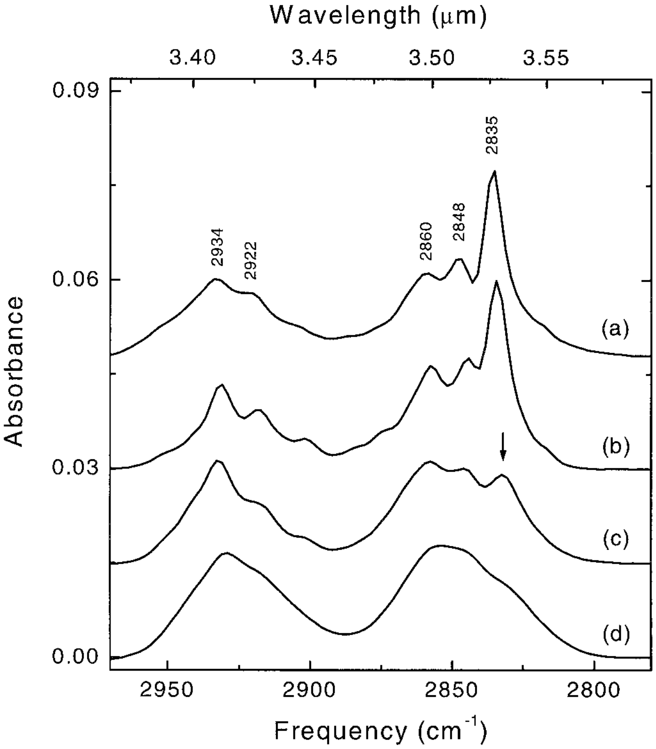

FIG. 3.—Comparison of the infrared spectra of diamond particles with a size of (*a*) 700 nm, (*b*) 100 nm, (*c*) 25–50 nm, and (*d*) less than 5 nm. The diamond nanoparticles are all derived from the same source and are H-etched using the same hot-filament method. All the spectra are taken at room temperature. The arrow in (*c*) indicates the emergence of the characteristic feature at 2835 cm^{-1}.

4. DISCUSSION

The present conclusion that the nanodiamonds around HD 97048 and Elias 1 should be larger than 25 nm is at variance with the estimate of Van Kerckhoven et al. (2002). We note, however, that in their estimation they considered only radiative loss of the energy (obtained from UV photon absorption) through surface CH stretches but neglected the two-phonon emission in the energy balance. While the two-phonon absorption of diamond at ~5 μm has a cross section about 3 orders of magnitude smaller than that of the surface CH stretches (Edwards & Philipp 1985; Cheng et al. 1997b), they can still make a significant contribution to the emission because their bandwidths are about 2 orders of magnitude larger than that of the CH stretches. The contribution of the bulk to the emission would become dominant as the fraction of carbon atoms on surface is less than 10% or the particle size is larger than 5 nm for a spheroid (Jones & d'Hendecourt 2000). With this factor taken into account, we conclude that the H-terminated diamond particles with a size larger than 10 nm can survive in the interstellar or circumstellar environments.

The size analysis in Figure 3 provides an additional support to the mechanism of interstellar diamond formation via a CVD-like rather than a detonation process (Daulton et al. 1996). The latter involves high-pressure shock metamorphism driven by high-velocity grain-grain collisions in interstellar shock waves associated with supernovae, transforming preexisting carbonaceous material to cubic diamond. However, such detonation-synthesized diamond grains have been predicted to have a size ranging from 0.5 to 10 nm (Tielens et al. 1987). According to the present findings, these nanodiamonds should not be large enough to produce the prominent 3.53 μm band, and the interstellar shock is therefore less likely to be responsible for the growth of the diamond grains around HD 97048 and Elias 1.

There are remaining some other details to be addressed in the spectra. For example, the absorption doublet at ~2930 cm^{-1} is better resolved when the diamond particles are treated by microwave (MW) rather than HF plasmas (Figs. 2*d* and 2*e*), and, remarkably, they match extremely well (particularly in relative intensity) with the astronomical observations. We attribute this observation to the result of proton etching since both H and H^+ are participating in the MW plasma reactions, whereas only H atoms are produced by the HF plasma. Such a selective etching effect of H^+ ions on non-(100)-oriented grains has been demonstrated by Zhang et al. (1997) in diamond film synthesis by MWCVD. Further examinations of these interesting points are currently underway in our laboratory.

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