

Activated C₇₀ and diamond

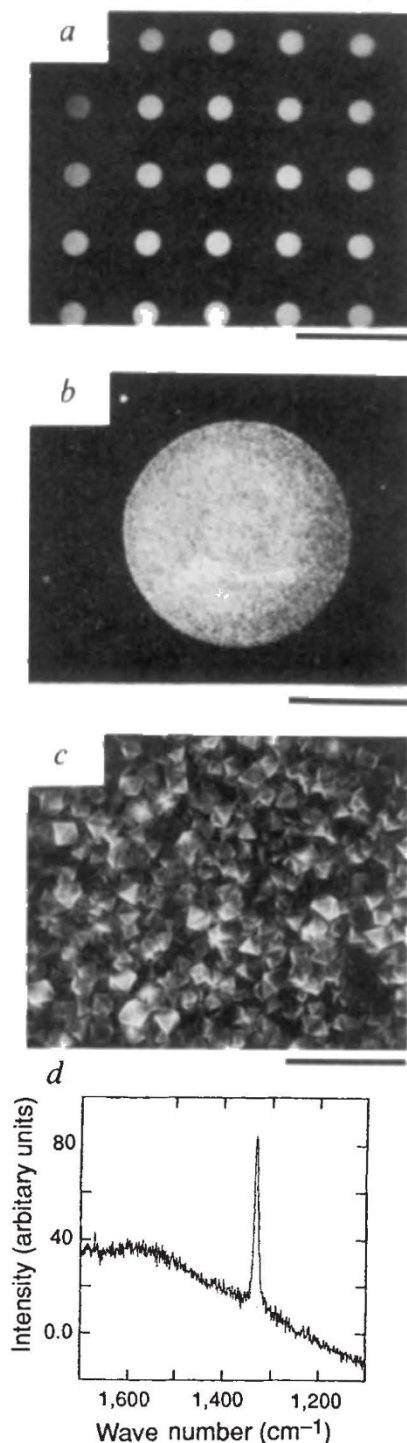
SIR — We have developed a novel method for nucleating high-density diamond crystallites by substituting thin, solid-film C₇₀ carbon clusters for diamond grit polish. Our method also allows for the one-step lithography of diamond growth in preselected areas.

Chemical vapour deposition (CVD) is a promising technique for growing diamond films on various substrate materials for protective coatings and the fabrication of active electronic and optical devices. To obtain high nucleation density of diamond crystallites on non-diamond substrates to form continuous films, a pretreatment of diamond grit polishing is necessary, which limits the full technological development of the CVD process.

In our experiments, 50–100-nm-thick films of pure C₇₀ have been thermally sublimated onto semiconductor-grade silicon wafers and other substrates (such as Mo, SiO₂). Diamond films are grown on these surfaces in a microwave (2.45-GHz) plasma reactor¹ with substrate temperature at 900°C and in a medium of 1% CH₄ in H₂ at about 100 torr total pressure. Unlike hydrocarbon molecules which are unstable in a hydrogen plasma, C₇₀ molecules are rather stable. Thus, we need to activate the cluster films for diamond nucleation, with a pretreatment of positive ion bombardment by biasing (200–300 V) the substrate with respect to the plasma. During the pretreatment (several minutes), the gas composition is 10% CH₄ in H₂ at 15 torr total pressure. Following this pretreatment diamond growth takes place. The figure (a) shows a scanning electron micrograph of diamond crystallites grown after activation on an array of 100-nm-thick C₇₀ dots on an Si substrate (formed by shadow masking) with a closer view of an individual dot in b. The figure also shows (c) the grain size (about 1 μm) and morphology of the resulting continuous (111)-oriented diamond film. The nucleation density in this film is comparable to that found on a diamond-grit polished Si substrate. Thus the amount of nucleation enhancement is close to 10 orders of magnitude relative to an untreated silicon surface. Other substrates, such as Mo and SiO₂, have also been used and show similar results. We have also used C₆₀ dots, but with less success (only a few orders of magnitude of enhancement). The Raman spectra of the diamond film (c) grown on activated C₇₀ are shown in d.

To assess the relative use of C₇₀ cluster films for diamond nucleation, we have used other forms of carbon such as diamond-like carbon, highly oriented pyrolytic graphite and polycrystalline

graphite. These forms enhance nucleation by only a few orders of magnitude under the same activation and growth conditions. In addition, we have found that hydrocarbon molecules, such as hydrocarbon-based oil and adamantane, are unstable in a hydrogen plasma, espe-



a, b, Diamond growth on 100-nm-thick C₇₀ dots (200 μm in diameter). c, Scanning electron micrograph of (111)-oriented diamond crystallites grown on a C₇₀ film. Scale bars: a, 0.75 mm; b, 100 μm; c, 10 μm. d, Raman spectra of the film in c.

cially above a temperature of 300°C.

From our experimental results we can speculate why C₇₀ is a unique precursor for diamond nucleation in a plasma CVD environment. Compared to other precursors, C₇₀ is more stable in a hydrogen plasma at high temperatures. Unlike graphite, C₇₀ provides spatially a third dimension (within the shell) to allow easy conversion from sp² bonding to sp³ bonding which is required for diamond nucleation and growth. Along the short axis perimeter of C₇₀ there are five ensembles of four hexagons which can be restructured to produce chair-form cyclohexane linkages. These linkages are representative of the surface of the 111-plane of diamond from which diamond can grow².

R. MEILUNAS

R. P. H. CHANG

Department of Materials Science and Engineering,

SHENGZHONG LIU

MANFRED M. KAPPES

Department of Chemistry,
Northwestern University,
Evanston, Illinois 60208, USA

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Carbon ratios in the Amazon

SIR — Despite the importance of the rainforests of the Amazon basin to greenhouse gas fluxes, terrestrial carbon storage and global biodiversity^{1,2}, there remains no consensus as to the nature of vegetation present in the region during the Last Glacial Maximum (LGM)³. Although there is broad agreement that the climate was cooler, opinions diverge on the question of glacial aridity in the region, and hence on the nature and extent of closed forest cover. The major barrier to resolving this problem has been that many proxy vegetation and climate records yield only fragmentary information which is poorly time constrained, and which pertains only to a localized region.

The carbon-isotope composition of organic matter in fluvial sedimentary sequences offers the possibility of investigating past vegetation changes on a basin-wide scale. The modern Amazon forests are almost exclusively dominated by plants which photosynthesize via the C₃ pathway, with δ¹³C values of about –28‰. In contrast, the more open ‘cerado’ vegetation (grassland/woodland) on the margins of the forest, contains a variable proportion of tropical grasses which photosynthesize via the C₄ pathway, yielding δ¹³C values of about