PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Local Epitaxial Growth of Diamond on Nickel from the Vapour Phase [and Comment]

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Local epitaxial growth of diamond on nickel from the vapour phase

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Deposition of diamond on nickel substrates has been performed by a microwave plasma reactor from methane–hydrogen gas mixtures. Growth features and the structures of the deposits have been studied as functions of methane concentration (0.3–5.0% (by volume)) and substrate temperature (700–1000 °C). At methane concentrations lower than 0.9%, diamond crystals, which have epitaxial relation to the substrate, have been observed to grow both on (111) and (100) faces of nickel. Other phenomena not observed with usual substrates have also been noted, and are believed to be caused by the unique properties of nickel.

1. Introduction

One of the characteristic features of the growth of diamond from the vapour phase is that diamond can be deposited in film forms on various non-diamond substrates. At present, however, what are known as diamond films are polycrystals. The necessity and advantages of single crystal films being obvious, attempts have been made to prepare single crystal films or epitaxial films on various non-diamond substrates.

Jeng & Tuan (1990) reported that clusters of oriented cubic nucleation of 1–2 μm and local epitaxial crystals of 120 × 150 μm on silicon {100} have been obtained by pretreating the substrate *in situ*, followed by usual growth process with a microwave plasma-assisted chemical vapour deposition. Koizumi *et al.* (1990) have reported epitaxial growth takes place on cubic boron nitride {111} surface by DC plasma chemical vapour deposition (CVD). Later, they found that epitaxy occurs on $\{111\}_B$ surface whose topmost layer is composed only of boron, while no tendency to epitaxy was observed with $\{111\}_N$ surface whose topmost layer consists entirely of nitrogen (Koizumi *et al.* 1991). Prins & Gaigher (1991) made an experimental study of ion implantation of carbon ions into copper and concluded that epitaxial diamond is formed at the surface by the precipitation of implanted carbon atoms under the influence of the substrate crystal structure. Stoner & Glass (1992) prepared what they termed textured diamond films on β–SiC by microwave plasma CVD preceded by *in situ* bias treatment that enhances nucleation. They found approximately 50% of the initial diamond nuclei are aligned with C(001) planes parallel to the SiC(001) plane.

This paper reports the results of further studies of the previous work (Sato *et al.* 1991), which showed for the first time that epitaxial diamond crystals grow on nickel

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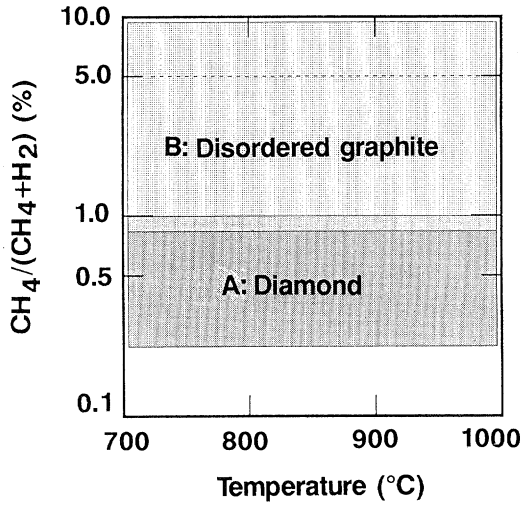

Figure 1. Schematic diagram of the relation between the deposition conditions and the structures of the deposits.

and cobalt substrates under appropriate gas compositions and substrate temperatures. Other phenomena characteristic to nickel substrates are also reported and discussed.

2. Experimental

A plasma reactor using microwave for excitation, similar to the one first adopted for diamond synthesis by Kamo *et al.* (1983), has been used for the growth studies. Briefly, it consists of a reaction chamber made of a quartz glass tube of 50 mm outer diameter, a gas feeding system, a simple mechanical pump for evacuation, and a microwave cavity connected to a microwave (2.45 GHz) generator. Gaseous mixtures of methane and hydrogen have been used for deposition. Nickel polycrystalline plates as well as (111) and (100) single crystals have been used as substrates. Deposition has been conducted under the following conditions: gas pressure within the range 40–100 Torr†; methane concentration within 0.2–5.0% (by volume); gas flow rate at 100 $cm^3\ min^{-1}$ (STP); and substrate temperature of 700–1000 °C.

The samples have been studied by optical microscopy, scanning electron microscopy (SEM), Raman spectroscopy and X-ray as well as electron diffraction. Raman scattering was measured with a Spex Ramalog 1403 with back scattering geometry. The 514.5 nm line of an argon ion laser was used for excitation.

3. Results

Structures of the deposits was found to be critically dependent on the gas composition as illustrated schematically in the diagram shown in figure 1, which was obtained at the gas pressure of 40 Torr. Similar diagrams as functions of the gas composition and substrate temperature (T_s) have been obtained in the range 40–100 Torr. Diamond crystals having epitaxial relation to the substrate have been observed to grow when the concentration of the methane gas was less than 0.9%

† 1 Torr ≈ 133 Pa.

Figure 2

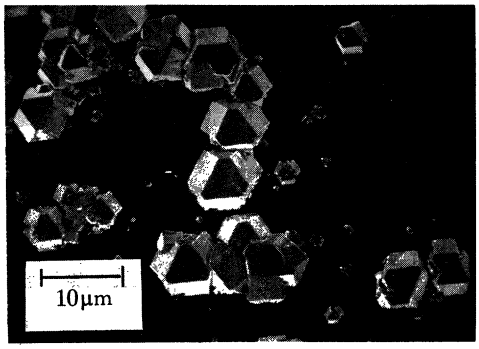

Figure 3

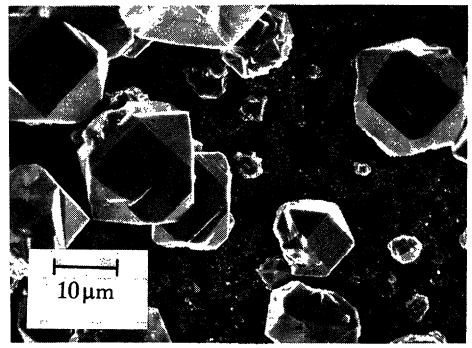

Figure 2. An SEM image of the epitaxial diamond crystals grown on (111) face of nickel grown at 0.5% methane, 100 Torr and substrate temperature $T_s = 880$ °C.

Figure 3. An SEM image of the epitaxial diamond crystals grown on (100) face of nickel grown at 0.5% methane, 60 Torr and at $T_s = 910$ °C.

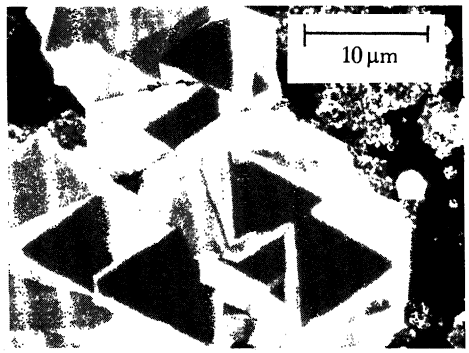

Figure 4. An SEM image of coalesced epitaxial crystals on (111) face, grown at 0.5% methane, 100 Torr and $T_s = 880$ °C.

(region A in figure 1), and when the methane content was higher than 1.0% the initial deposits were found to consist entirely of disordered graphite, or soot-like carbons (region B in figure 1). In the region B at a methane concentration of 1.0–1.5%, separate diamond crystals started to grow after the substrate surface was covered with a layer of the soot-like carbons with thickness of 0.1–1.0 μm. No tendency to epitaxy has been observed with these crystals. Results similar to the above have also been observed with cobalt polycrystalline substrates.

(*a*) *Local epitaxy and coalescence of crystals*

For the samples prepared in region A of figure 1, individual diamond crystals were found to grow epitaxially on (111) face as well as on the (100) face, as shown in figures 2 and 3 respectively. X-ray measurements by Laue method showed that they are epitaxial with respect to the substrate plane within the experimental error of about 2°. Various observed orientations of crystals found on different grains of polycrystalline nickel plates suggests that diamond grows epitaxially on crystallographic planes other than (111) and (100) planes, but the determination of other planes has not been made. From SEM observation, it was noted that there are crystals which have no epitaxial relation to substrate. The probability of finding

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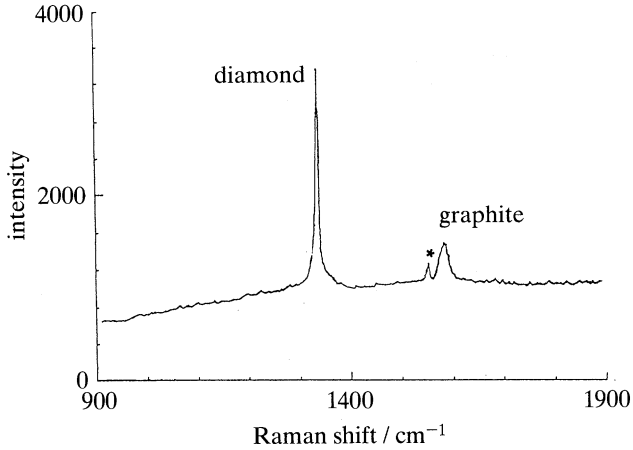

Figure 5. Raman spectrum of epitaxial diamond grown on (111) face. The smaller peak at 1580 cm^{-1} is due to well-crystallized graphite and a weak but sharp peak with asterisk is due to oxygen molecules in air.

these crystals decreases as the substrate temperature increases, and the samples prepared at a substrate temperature higher than about 880 °C are substantially free from non-epitaxial crystals.

As shown in figure 4, coalescence of epitaxial single crystals takes place where the nucleation density is high, leading to a larger single crystal area. The nucleation behaviour appeared to be similar to that of the substrates which are widely used, e.g. silicon, molybdenum, tantalum and tungsten. Surface treatments with hard abrasive powders, in particular diamond, were found to be effective in increasing the nucleation density. It has been noted that the nucleation density is lower for the samples deposited at higher substrate temperatures.

The Raman spectrum of an epitaxially grown crystal is shown in figure 5. The sharp, strong line at 1333 cm^{-1} is due to diamond (Solin & Ramdas 1970) and a weak peak at 1580 cm^{-1} is assigned to well-crystallized graphite (Tuinstra & Koenig 1970; Nemanich & Solin 1979). The line width observed with a number of crystals expressed as full width at half maximum (FWHM) was found to be within 1.8–2.0 cm^{-1}.

(*b*) *Disintegration of crystals*

A phenomenon that we have not encountered so far with other substrates of various types, including silicon, tungsten, tantalum, molybdenum, copper, silica, alumina, some carbides and nitrides, has been noted with nickel as well as cobalt. A crystal once grown epitaxially disintegrates into smaller fragments of epitaxial crystals and tend to disappear. This has been noted when deposition was interrupted for the inspection of the sample and then the deposition was resumed. After the second run, crystals that had grown in the first run was found to disintegrate as shown in figure 6. Similar crystals have been also found after a long deposition run of about 40 h or more.

(*c*) *Formation of well-crystallized graphite*

Formation of a thin but visible layer has been often noted at the back side of the substrate which faced the surface of the sample holder made of silica glass. It appeared that thicker layers were formed when the deposition was conducted at

Figure 6

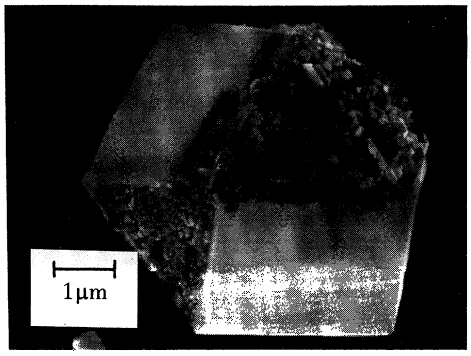

Figure 7

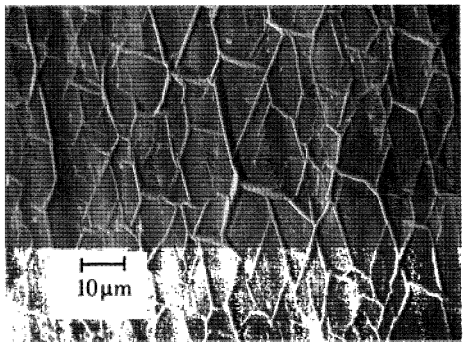

Figure 6. An SEM image of a partly disintegrated crystal.

Figure 7. An SEM image of well-crystallized graphite layer formed at the back side of nickel substrate which has been subjected to deposition at 0.5% methane, 100 Torr and $T_s = 980$ °C.

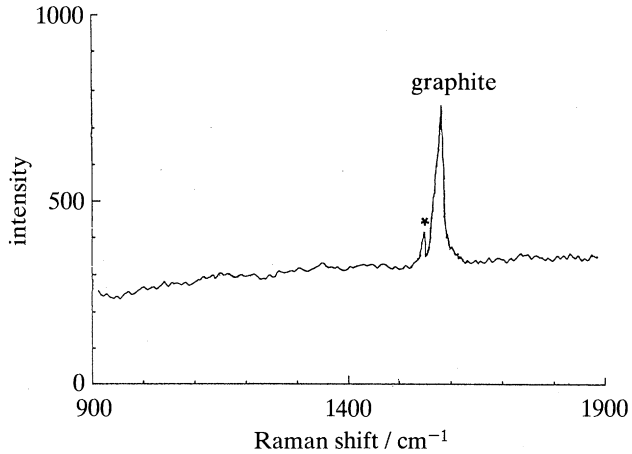

Figure 8. Raman spectrum of the graphite layer formed at the back side of the substrate under the same condition as that of the sample shown in figure 7.

higher temperatures. An SEM image is shown in figure 7 and the Raman spectrum of the layer in figure 8, which consists of a single sharp line at 1580 cm^{-1}, indicating that the layer is well-crystallized graphite. It has also been shown that the top surface of the substrate, where diamond deposits, are also covered with a very thin layer of good quality graphite which is normally invisibly thin but gives an appreciable Raman signal, as seen in figure 5. Raman microprobe measurements indicated that a thin graphite layer is also present at the interface of diamond and substrate.

4. Discussion

It has been shown that individual crystals having epitaxial relation to the substrate grow when the gas composition is controlled below the critical methane content of about 0.9%. Further, the possibility has been shown that the coalescence of these crystals can take place to form a single crystal film.

It has also been shown, however, that diamond crystals start to disintegrate into smaller crystals after interruption or after a prolonged reaction and this disturbs an

extensive growth and coalescence of crystals. Here, a brief discussion will be given of the possible causes of anomalous phenomena observed with nickel and also of the future directions.

(a) *Causes of anomalous deposition features*

Apart from the epitaxial growth of individual crystals, anomalous reaction features have been noted. One is the fact that when the methane content is higher than about 1.0%, the initial deposits consist entirely of disordered graphite (region B of figure 1). The abrupt change in structure from diamond to graphite within a narrow range of about 0.1% is in sharp contrast to the gradual changes in the fraction of graphite content as a function of methane content (or carbon content, in general) in the gas phase observed with most of the well-known substrates (see, for example, Sato & Kamo 1989; Bachmann *et al.* 1991).

The other anomaly is the disintegration of diamond crystals. Though no definite conclusions have been drawn as to the causes of these anomalies, it seems certain that they are related to the unique properties of nickel, of which those relevant to the present work may be summarized as follows. In the temperature range of the present deposition experiments (700–1000 °C), nickel is known to show, (i) catalytic activity to carbon–hydrogen compounds, (ii) high solid solubility to carbon which increases with increasing temperature, (iii) high diffusion rate of carbon, (iv) very high diffusion rate of hydrogen and (iv) little tendency to form stable carbides.

The formation of disordered graphite at a relatively low methane concentration of about 1.0% may be caused by enhanced rate of carbon deposition resulting from the catalytic activity of nickel. It may be plausible to think that the deposit on nickel has a structure corresponding to that of the deposit on silicon prepared from a mixed gas of much higher methane concentration due to the catalytic activity.

One of the probable mechanisms of disintegration of diamond crystals is that it is caused by the transport of carbon atoms from diamond to graphite through nickel, since the free energy of diamond is higher than that of graphite. As described above, well crystallized graphite is found at the back side of the substrate. The graphite can be formed on gradual cooling after the microwave power is turned off. Thus the subsequent deposition run with the same sample will certainly be subject to this mechanism. If graphite is also formed while deposition is conducted, it explains the degradation in prolonged deposition runs.

As immediate technical approaches to prevent the graphite formation, the following have been considered: (i) to expose the whole surface area of a substrate to the gas plasma; and (ii) to minimize temperature variation as functions of reaction time and position of the substrate. For extensive coalescence, increase of nucleation density and increase of growth rate will be effective.

In the above discussion, it is postulated that a thermodynamical equilibrium approach is valid inside the substrate. On the other hand, it may be obvious that kinetic principles predominate in the reactions occurring at the surface and in the gas phase near the substrate surface where a sharp gradient in temperature exists.

(b) *Advantages of nickel substrates*

It is possible to point out some advantages in using nickel as substrates even at this stage, where the technique still needs further developments. (i) It is feasible to obtain large area single crystal substrates by various ways that include growth of bulk crystals and epitaxial films. (ii) It is feasible to attain a close matching of the lattice

parameters at a deposition temperature by alloying with other metals and elements, thus enabling to obtain epitaxial films substantially free from dislocations coming from the lattice parameter difference. (iii) Epitaxial diamond films will be readily separated from the substrates by intentional precipitation of graphite at the interface of nickel and diamond, thus allowing repeated usage of the bulk single crystal substrates, and ready transfer of the films onto other substrates for further growth and/or manipulation.

We believe that the epitaxy on nickel and its alloys is worth further study. Because of the seemingly complex reactions involved with nickel, as discussed above, it is planned to make experimental studies to elucidate some of the fundamental processes in the reactions and transport phenomena, together with technical approaches, also suggested above. The same may be concluded for cobalt.

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Comment

M. Seal (*Sigillum B.V., Amsterdam, The Netherlands*). A possible way of avoiding the loss of the epitaxial diamond film through dissolution in the nickel is the following. After formation of the initial oriented diamond layer, stop the diamond growth and deposit a different support film (e.g. silicon) over the growth surface. Dissolve or release the nickel, and remove the graphite and any residual nickel from the lower surface of the diamond by chemical or ion etching. One might then be left with an oriented diamond layer on a silicon substrate, which could be thickened, hopefully epitaxially, by any of the standard diamond CVD techniques.

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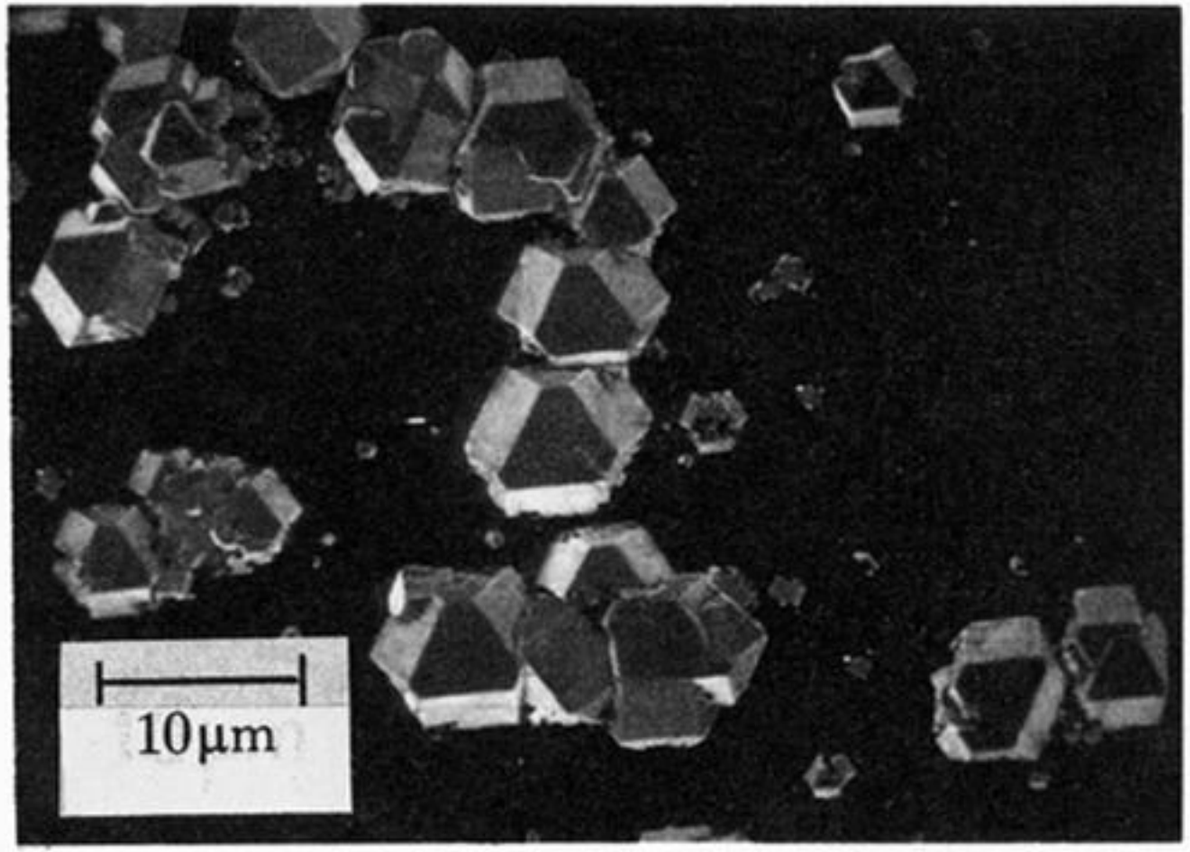
Figure 2



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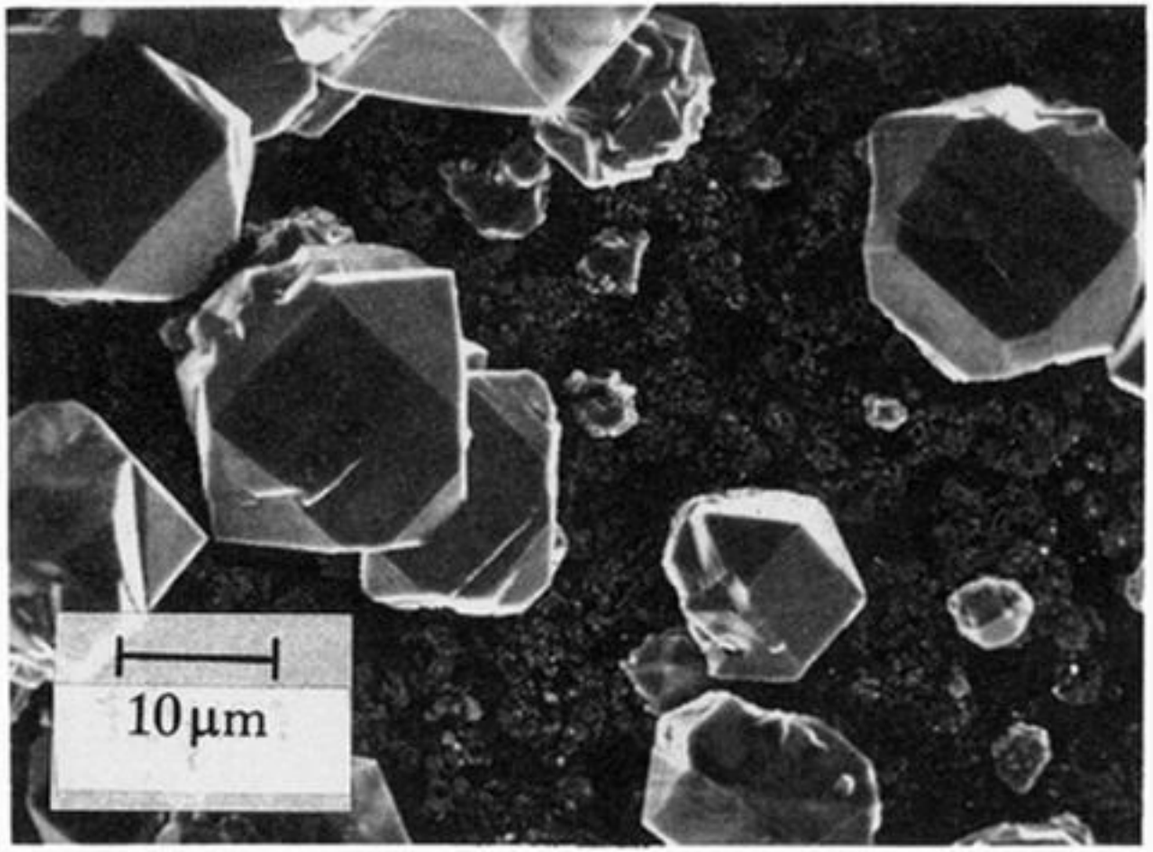

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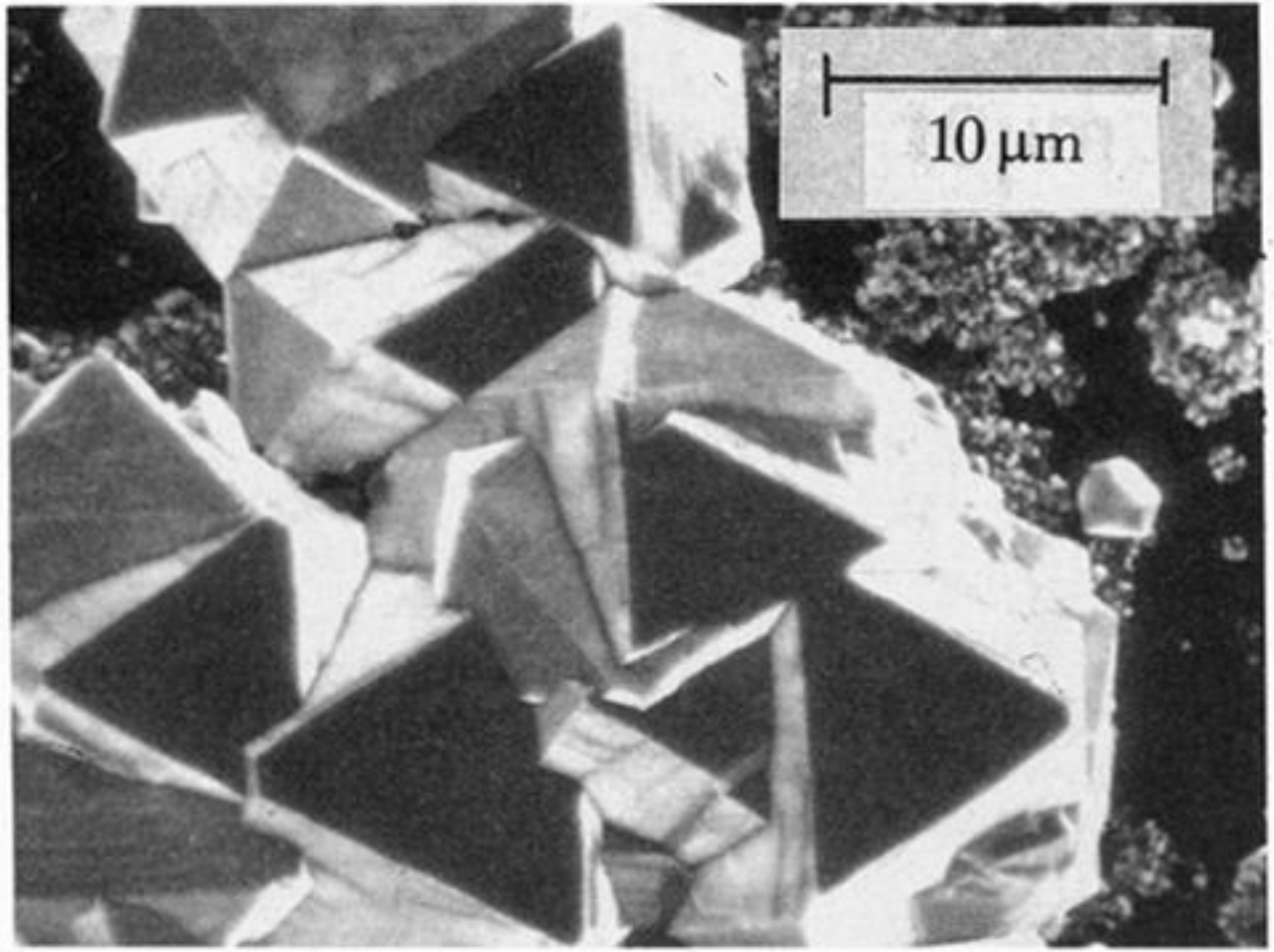

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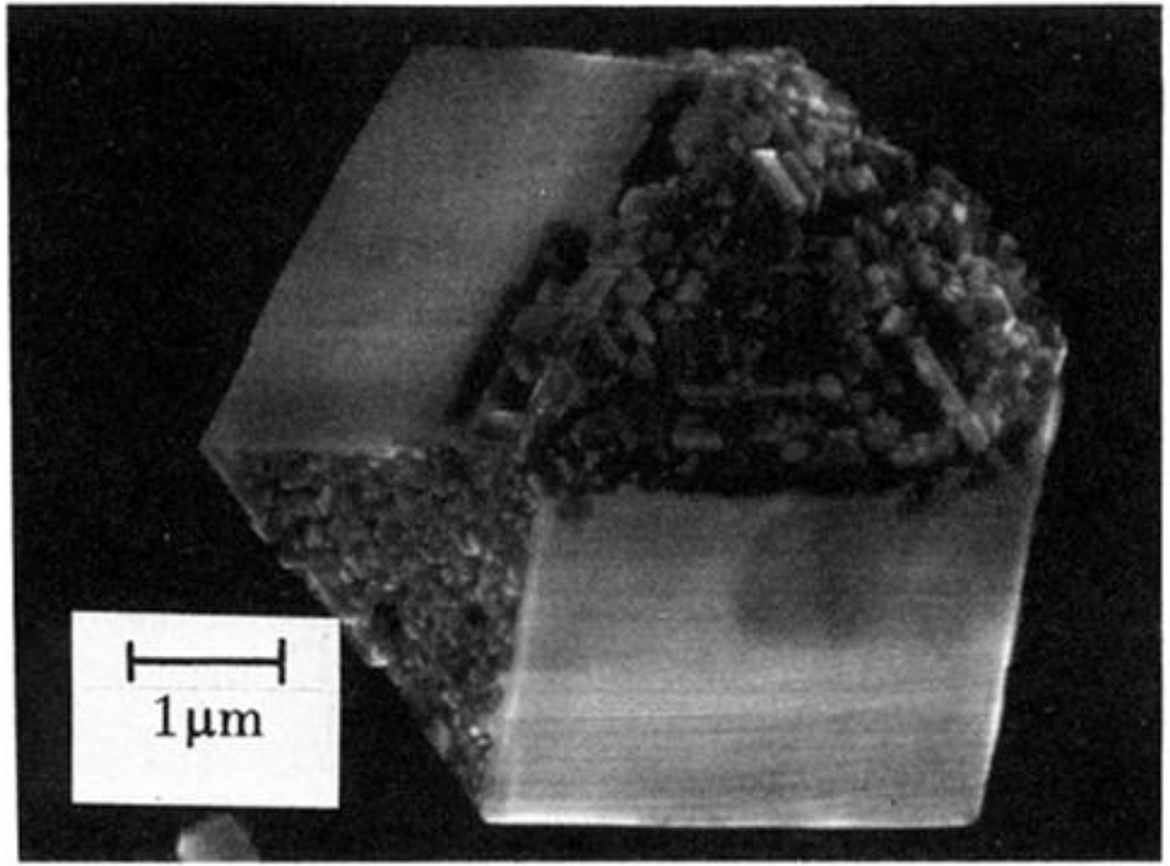

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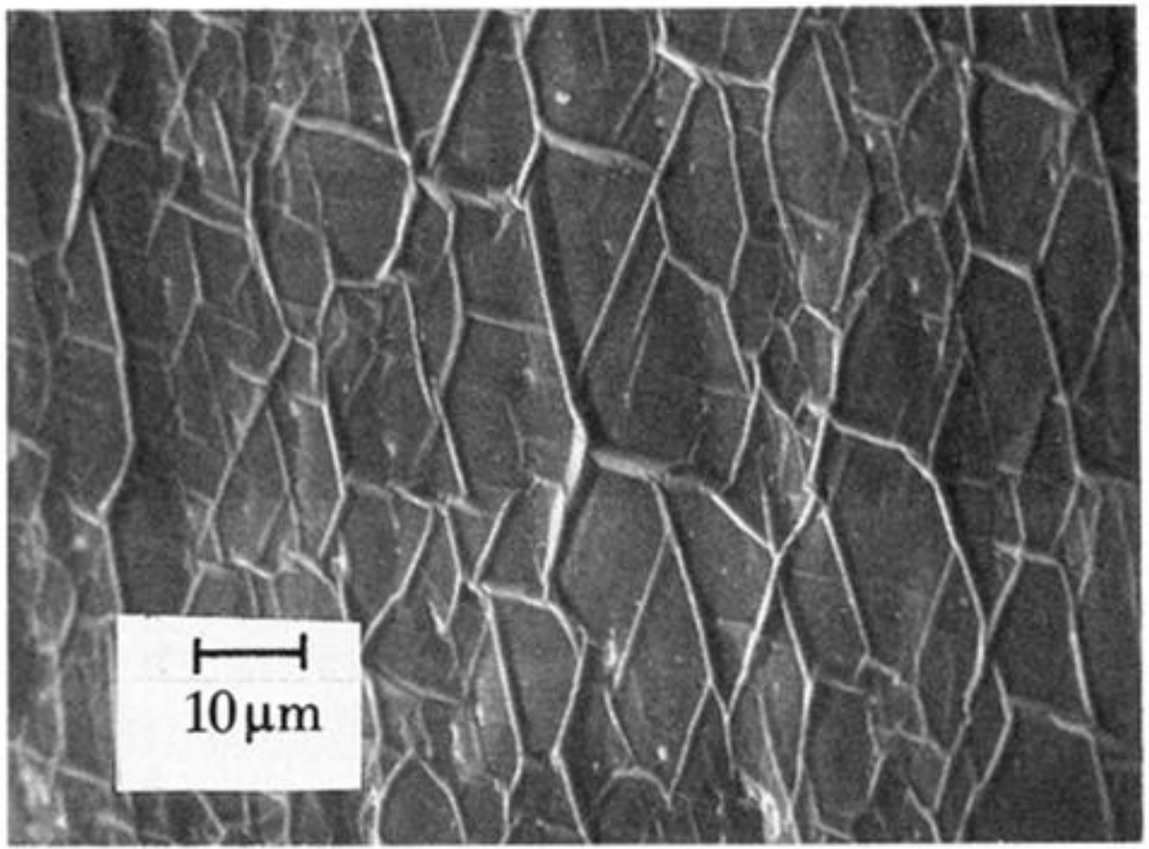

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