

Selective Patterned Deposition of Diamond using a New Technique

Liya L. Regel* and William R. Wilcox

International Center for Gravity Materials Science and Applications

Clarkson University, Potsdam, New York 13699-5814, USA

The objectives of this research were to achieve selective patterned deposition of diamond and to determine the influence of centrifugation on diamond deposition.

It is generally believed that atomic hydrogen at the growth surface is required for chemical vapor deposition of diamond films [e.g., 1,2]. Typically, atomic hydrogen is generated either by a hot metal filament or by a plasma at low pressure. Angus [3] stated that in the low pressure processes (e.g., microwave and hot-filament-assisted deposition) the transport is entirely dominated by molecular diffusion. Convection plays virtually no role.

The previous methods used for diamond deposition were unsuitable for experiments on a centrifuge. Thus, a new closed chemical vapor transport reactor was developed that could deposit diamond films over an extended time without continual addition and removal of gas [4]. Graphite was used as a carbon source in the presence of hydrogen at low pressure, without a catalytic filament. Figure 1 shows a schematic diagram of the apparatus. Power applied to the 25 x 2 x 2 mm graphite rod is regulated via a variable autotransformer. The substrate is located a few mm from the graphite rod, crosswise to it, and either above or below it. The chamber is closed, evacuated, and flushed several times with hydrogen. The valve is closed with a hydrogen pressure ranging from 30 to 100 Torr in the chamber. Electric power to the graphite rod is slowly increased until the desired voltage is reached. The substrate is heated by radiation from the graphite rod and by hydrogen atom recombination [5]. We determined the influence of the voltage applied to the graphite rod, the rod - substrate spacing, the geometry, the hydrogen gas pressure, the temperature - time cycle, etc. The optimal conditions depended on the substrate and the desired morphology of the deposit [6]. Diamond growth rates were comparable to those using hot filament chemical vapor deposition (several $\mu\text{m/hr}$). The Raman spectra of the samples had a single large peak at 1332 cm^{-2} , showing that they were high quality diamond.

Initial tests of the new technique were performed on 2 mm thick single crystal silicon that was 2 cm long and either 1.5 or 2 cm wide. The substrate was clamped at the ends by tungsten holders and placed in the deposition chamber near the graphite rod. The resulting microstructures ranged from isolated twinned crystals to complete coverage over about 2 cm^2 area. The best deposits on roughened substrates were obtained with a starting gas pressure in the chamber of 50 Torr hydrogen, a reaction time of at least 30 min, a substrate temperature of 738°C , and the substrate placed 2.5 mm below the graphite. Figure 2a shows a typical deposit. Duplicate experiments were performed on our large centrifuge HIRB [7]. The deposition chamber was mounted inside a swing bucket attached with a hinge to the end of a 1.5 m radius arm on a rotating table. In this way, the axis of the growth chamber was always aligned with the net acceleration vector. With centrifugation to a net acceleration of 2.5 times earth's gravity ($2.5g$), nucleation, growth kinetics, and the area covered were all strongly increased (e.g., Figure 2b).

Patterns are necessary for applications of diamond films to microelectronic and micromechanical devices [8]. Another promising application for patterned diamond is cold-cathode field emitters [9],

* Corresponding author. Fax: 1-315-268-3833. Email: regel@agent.clarkson.edu

e.g., for low-power flat panel displays [10]. Diamond can operate as an electron emitter with anode voltages of 400 V at pressures in excess of 100 Pa of nitrogen without damage [11]. Previously, patterned diamond films had been obtained by the following procedures:

- Selective deposition on silicon abraded by diamond powder using chemical vapor deposition (CVD) [8,11].
- Masking of diamond-abraded Si by SiO₂ or Si₃N₄ and then depositing diamond by CVD [8].
- Use of patterned SiO₂ or Si₃N₄ to prevent etching of diamond by O₂ at 700°C [8].
- Squeegee deposition of diamond grit slurry into holes in SiO₂ on Si, followed by heating at 1080°C [9].
- Deposition of diamond with selected areas coated with material on which diamond does not deposit by CVD [11].
- Selective CVD on Si-rich nitride patterned on negatively biased silicon [12].
- Deposition through metal-foil shadow masks using pulsed laser ablation [14].
- CVD only on areas first coated with Ni on graphite [14].

Patterned emission from a completely coated surface was achieved by treatment of selected areas before deposition in order to enhance the emission characteristics of those areas [10].

Here, deposition was carried out on a silicon wafer onto which a thin layer of silicon oxide had been grown thermally. On the silicon oxide was a test pattern (Fig.3) of ~ 1 μm thick copper, under which a ~ 0.05 μm layer of titanium had been deposited for improved adhesion. This substrate was cleaned in an ultrasonic bath, alternating between ethanol and acetone. The surface was not contacted with diamond powder.

Ten deposition experiments were performed with the graphite heater rod placed 2.5 mm above a 2 cm x 2 cm patterned substrate, an initial hydrogen pressure of 30 to 60 torr, and a substrate temperature of 730 to 750°C. Scanning electron microscopy showed the usual faceted crystals, while energy dispersive x-ray spectrometry showed the presence of Cu and Ti only under the diamond. Tape adhesion tests removed none of the deposits.

Although selective deposition on copper was obtained in all experiments, the best results were obtained at an initial hydrogen gas pressure of 50 torr and a substrate temperature of about 740°C. A deposition time of 60 min gave a continuous film on the copper, over 70% of the 4 cm² area of the substrate. Figure 4 shows that the resolution of the deposited pattern was about 1 μm, being limited by the size of the diamond crystals.

Five deposition experiments were also carried with centrifugation. Unlike deposition without centrifugation, during deposition the pressure and substrate temperature increased dramatically. Again, diamond deposited selectively on the copper pattern. Figure 5 compares typical deposits obtained with and without centrifugation. At an acceleration of 2 g under the same conditions used without centrifugation, the portion of the substrate area covered by diamond increased to about 90%.

Interestingly, we deposited diamond on glass substrates under almost the same conditions as used for selective deposition on a copper pattern on SiO₂. That is, when only SiO₂ was present, diamond deposited on SiO₂, whereas in the presence of patterned copper it did not. We believe that this anomalous behavior resulted from the character of the present CVT method in contrast to the previous CVD methods. In CVD, a dilute mixture of CH₄ in H₂ flows through the chamber, and a hot filament or plasma is used to generate CH₃ and H radicals. These are the primary species thought to be responsible for deposition of diamond. In the present CVT method, CH₃ and H must be generated at the surface of the hot graphite rod. These species are then transported by diffusion and buoyancy-driven convection to the substrate, where their concentrations increase until

diamond nucleates and grows. This growth consumes the CH_3S , and probably also catalyzes the conversion of HS to H_2 , causing their concentrations to decline to the level at which growth continues while nucleation is reduced or halted. In other words, unlike CVD, the CVT process is self regulating. In CVD, the CH_3S and HS concentrations are primarily determined by the feed gas composition, flow rate, etc., making nucleation much more sensitive to these conditions. Thus, we believe, in the present selective deposition, CH_3S and HS increase until nucleation of diamond occurs on the copper. Subsequent growth of diamond lowers the concentrations of CH_3S and HS so that nucleation cannot occur on SiO_2 , where higher concentrations are required for nucleation than on copper. On the other hand, if Cu is not present, the buildup in CH_3S and HS continues until nucleation does occur on SiO_2 .

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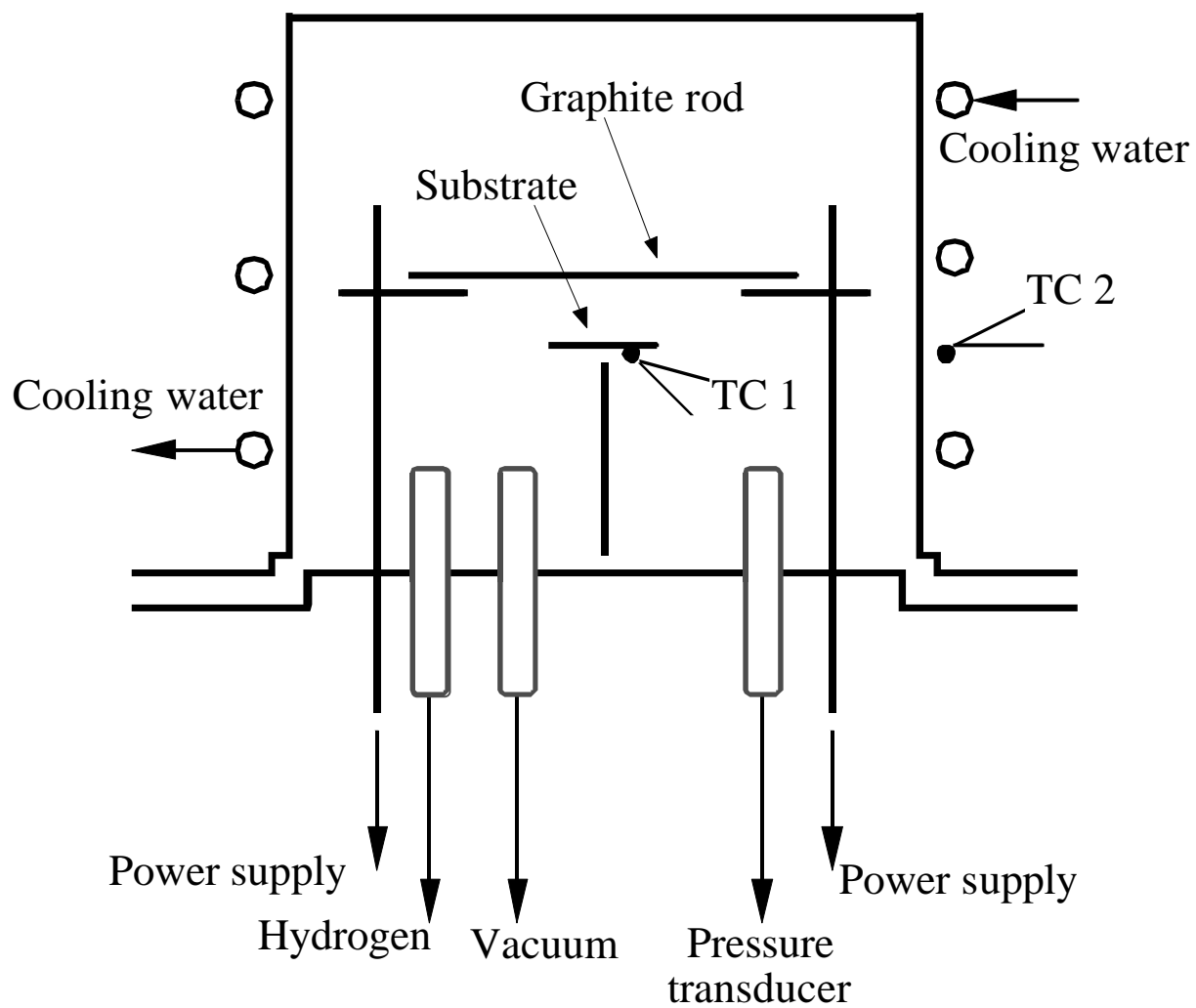


Figure 1. Schematic diagram of apparatus for chemical vapor transport of diamond.

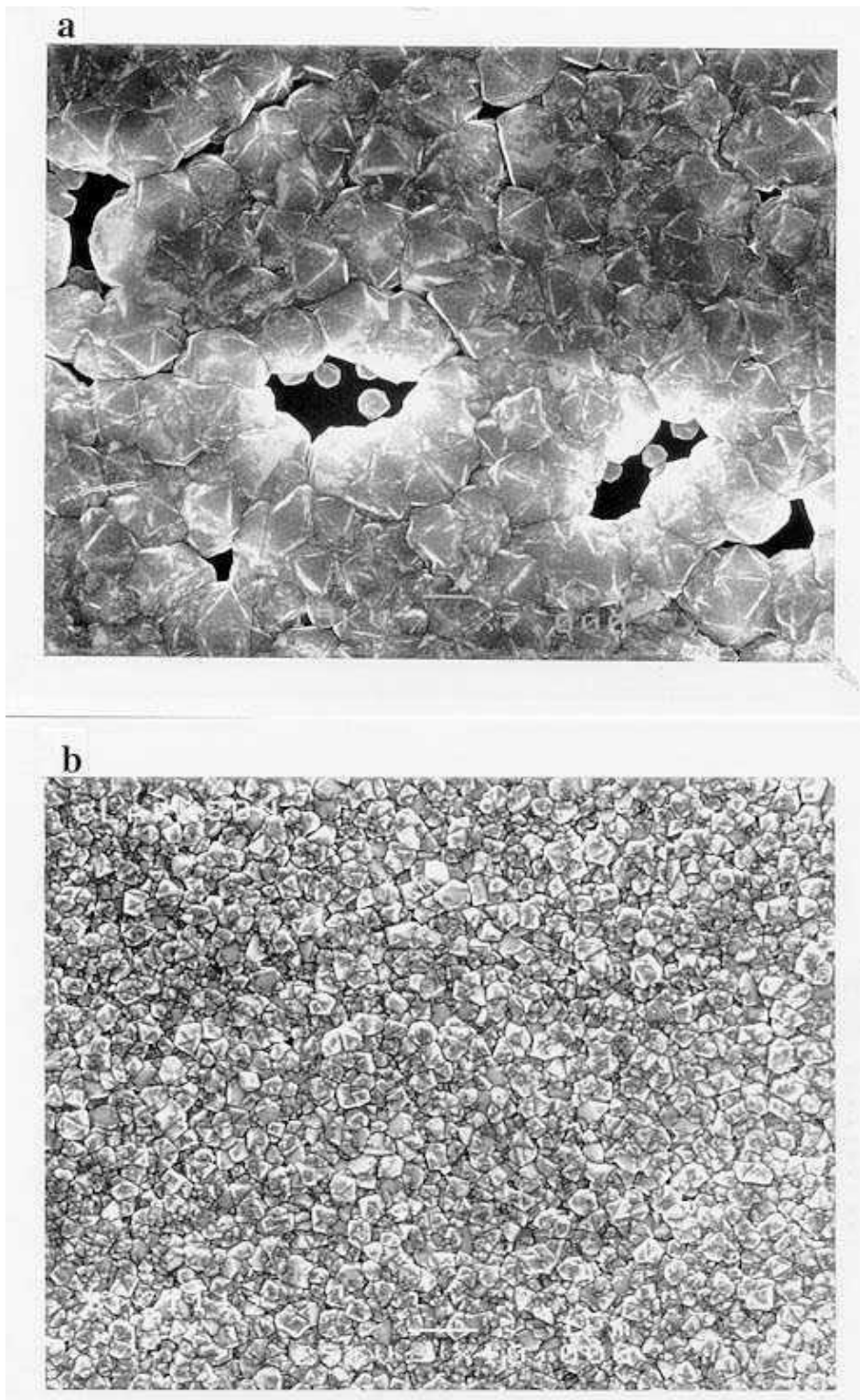


Figure 2. Scanning electron micrographs of diamond deposited on roughened (111) silicon substrates for 40 minutes by the new closed-chamber technique without (a) and with (b) centrifugation at 2.5 g , under otherwise identical conditions.

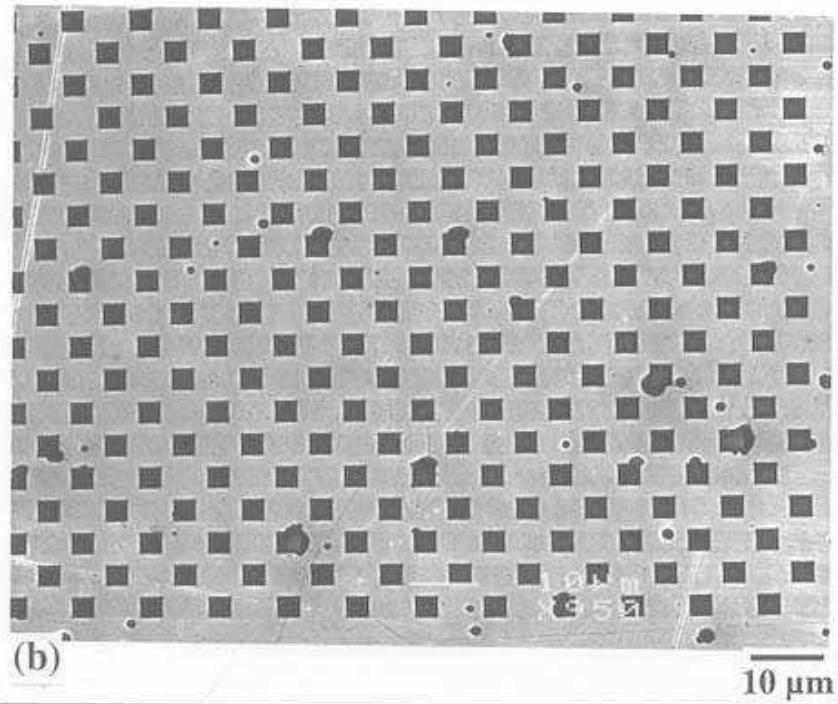
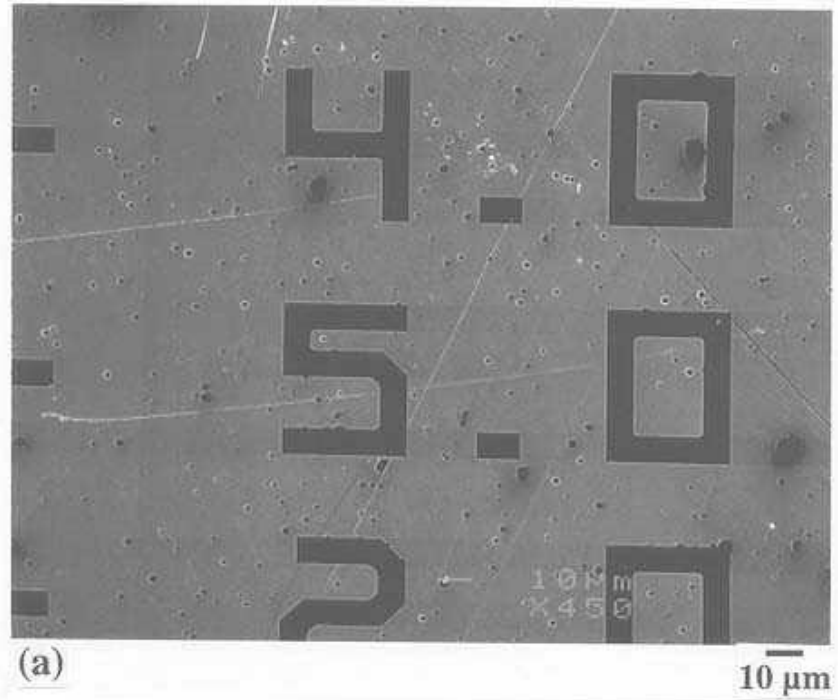


Figure 3. SEM photographs of typical patterned silicon wafers. The light areas are copper while the dark areas are silicon dioxide.

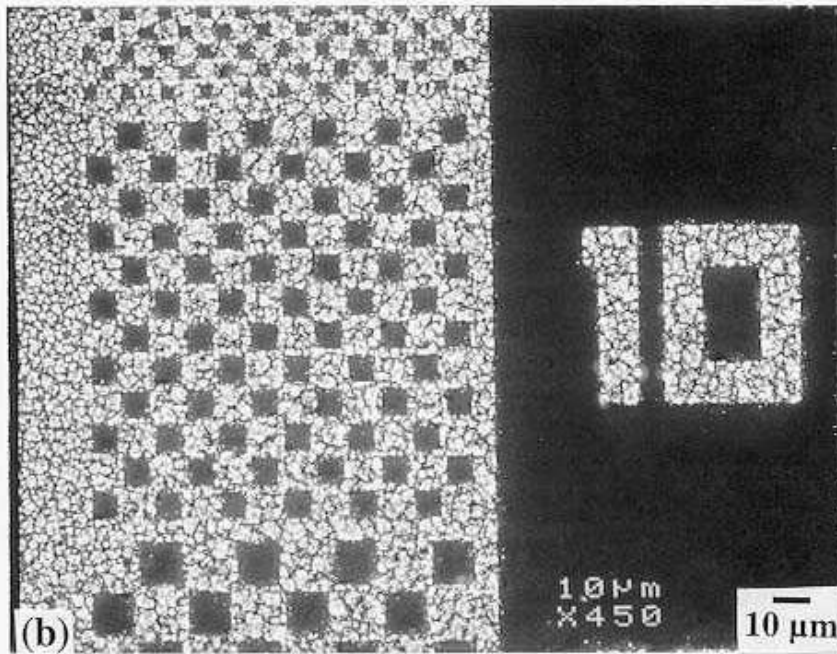
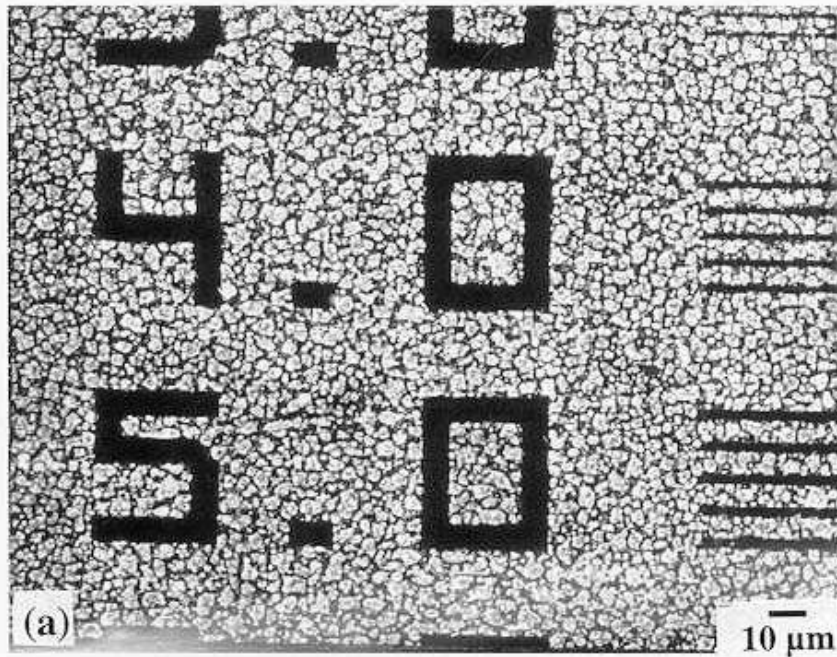


Figure 4. SEM photographs of selective patterned deposition without centrifugation. The bright areas are diamond on copper, while the dark areas are bare silicon dioxide. (a) Initial hydrogen pressure 30 torr, deposition time 45 min. (b) Initial hydrogen pressure 50 torr, deposition time 45 min.

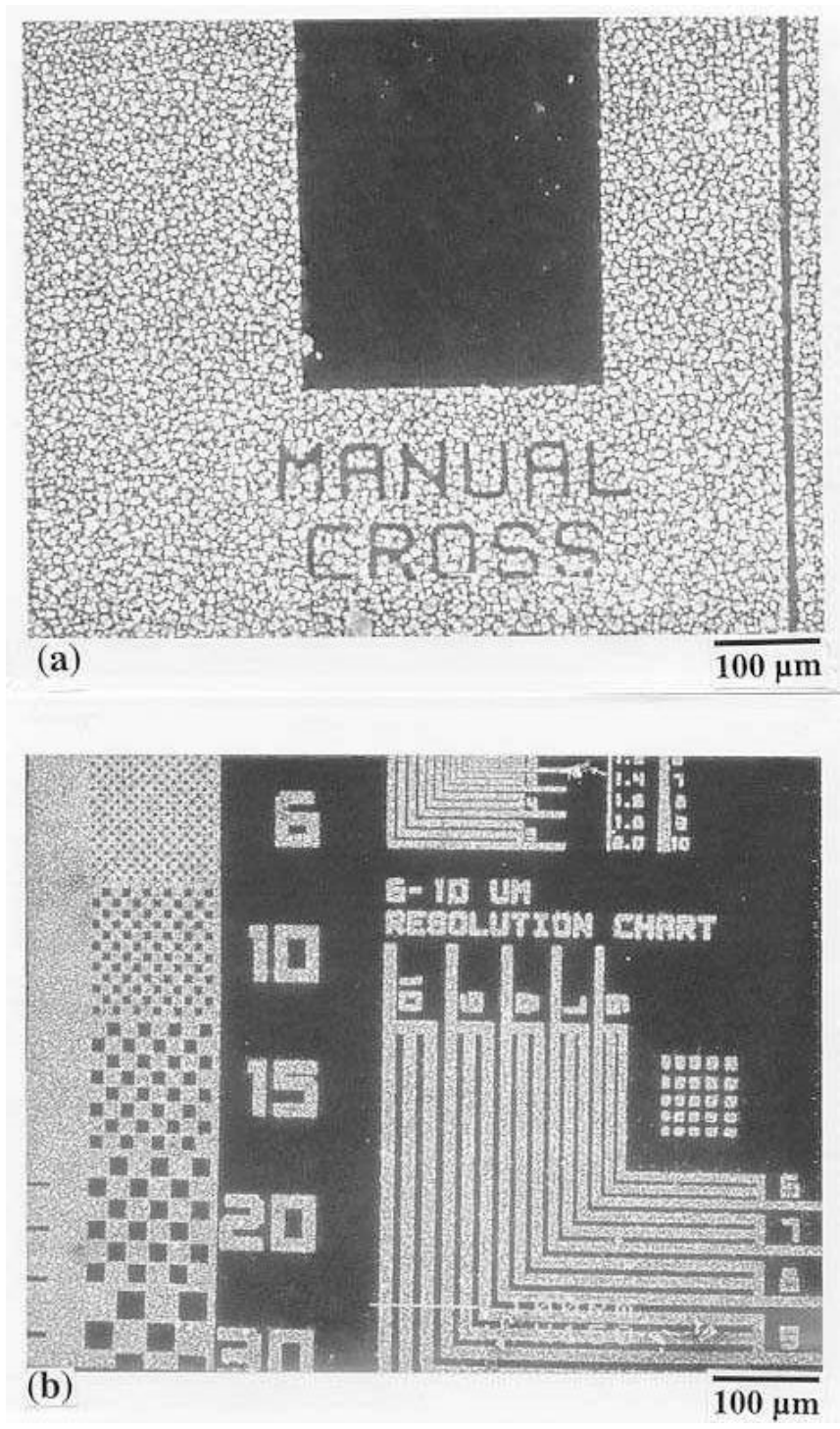


Figure 5. SEM photographs of selective deposition of diamond on copper with an initial hydrogen pressure of 50 torr and a deposition time of 60 min. (a) Without centrifugation. (b) With centrifugation at 2g.