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Microwave plasma chemical vapor deposition of diamond films with low residual stress on large area porous silicon substrates

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Abstract

Diamond films were deposited on 3-inch diameter p-type ⟨100⟩ oriented porous silicon substrates using a microwave plasma disc reactor. Thin porous silicon layers were obtained on silicon wafers by anodization in an $H_2O/HF/C_2H_5OH$ solution. Process parameters were varied to obtain the best quality uniform porous silicon films. Diamond films were deposited on these substrates with and without dry seeding techniques utilizing 4-nm diamond particles. Power and pressure were varied in the range of 2800–3300 W and 50–60 Torr, respectively, while the methane concentration was kept constant at 1% by volume in hydrogen. Diamond was successfully deposited on anodized silicon substrates without dry seeding. However, the films were discontinuous in certain regions even after 20 h of deposition and the deposition rate was low. Dry seeding of the porous silicon surface yielded a high deposition rate and uniform films. Porous silicon was found to reduce the intrinsic stress in the deposited diamond film considerably. Furthermore, film adhesion was also improved with porous silicon.

Keywords: Microwave plasma chemical vapor deposition; Diamond films; Porous silicon

1. Introduction

Diamond is one of the most precious materials found on the surface of earth. It has many desirable electrical and mechanical properties suitable for many high-tech engineering applications. The unmatched physical properties coupled with the ease with which diamond can be synthesized at low temperatures and low pressures, gives diamond a vast range of industrial application in the fields of optoelectronics, and mechanical and chemical engineering. As the cost of synthesis goes down and the volume production goes up, diamond can offer simple solutions to the problems encountered in complex electronic systems. Its high thermal conductivity, good mechanical strength, and good electrical insulation property make diamond an ideal substrate for high density, high power electronic packages. Diamond has a very low coefficient of thermal expansion (CTE), and a low dielectric constant which gives it an added advantage in the microelectronics packaging industry. Diamond has a very low loss tangent and very good transparency over a broad optical spectrum, which makes it suitable for use in radome applications in dual or multispectral electromagnetic systems. Diamond has a high dielectric strength and a higher charge carrier velocity than any other semiconductor. This renders it most useful in microwave power amplifier applications [1].

The nucleation density of diamond on heterogeneous substrates is very low. Silicon is the most common substrate used for diamond deposition. A certain pre-treatment of the silicon substrate before depositing diamond enhances the nucleation density considerably. Dry polishing is a promising technique for getting a uniformly seeded diamond layer, but that alone may not give sufficiently high nucleation density. Therefore, we investigated the use of a fine layer of porous silicon to provide nucleation sites on a silicon substrate by trapping diamond seed particles in its nanometer-size pores. The results show a good nucleation density, as well as uniform diamond deposition on porous silicon samples.

2. Porous silicon

A porous silicon layer consists of nano-pores or deformities formed on top of the silicon substrate. These pores may act as preferred sites for nucleation of diamond. A porous silicon surface also has many hydrogen-terminated atoms which readily react with CH_3 radicals in a methane plasma to form SiC-type bonds by hydrogen abstraction [2]. Once a carbon layer is formed on top of the porous silicon coated substrate, nucleation is expected to be fast. A further advan-

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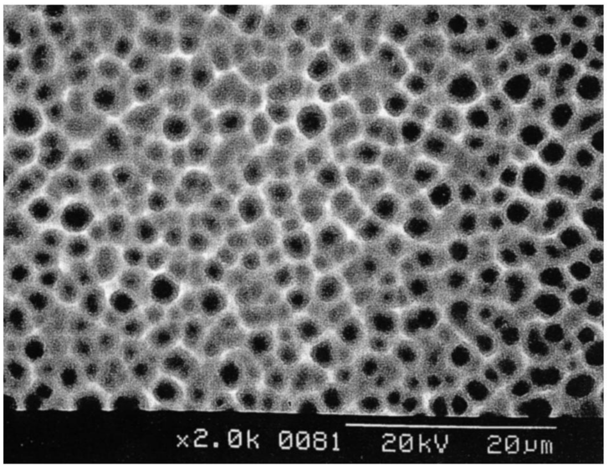

Fig. 1. SEM of porous silicon after anodization at $J_a = 150$ A/m^2 for 30 min.

tage of a nano-structure porous silicon surface comes from its ability to hold nano-size diamond particles during dry polishing. 'Dry polishing' is a simple technique in which dry diamond particles are rubbed on the silicon substrate with lint free paper. Fine (nanometer size) scratches are created uniformly on the surface of the wafer which are also heavily loaded with these nanometer size diamond particles. These scratches plus the diamond powder left behind on the substrate act as nucleation sites, thus increasing the nucleation density. Porous silicon has 600 times more surface area compared to an untreated polished silicon wafer [3]. This means that its surface would be loaded to the maximum with diamond particles after dry polishing. In fact, the surface coverage may be even higher than 100% under ideal loading conditions since the surface area of porous silicon is much higher than that of polished silicon. Also, if the same size pores are generated uniformly over the entire silicon surface, the diamond particles trapped in the pores after dry polishing would be uniformly distributed. A porous silicon layer is a spongy material. It has many Si dangling bonds on its surface which are ready to form chemical bonds with other atoms, such as carbon, and thus, has great potential to increase diamond nucleation. The porous silicon layer could also reduce biaxial stress in the growing diamond film due to its increased surface (and interface) area and its morphology. Being spongy, it is expected to be more compliant as well. At the same time, these properties of porous silicon are expected to yield higher adhesion between diamond and silicon. All these characteristics are attractive for applications where diamond on silicon is utilized.

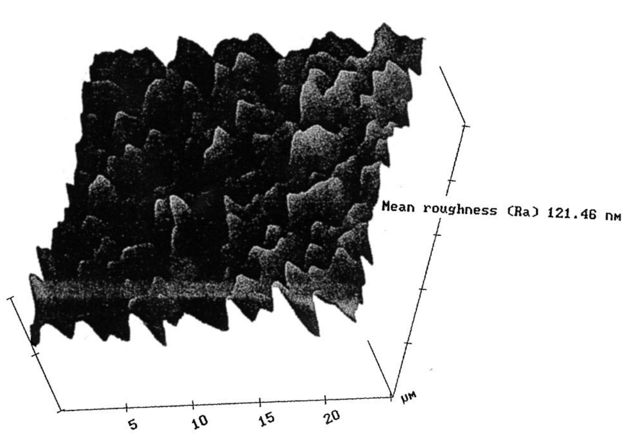

Fig. 2. AFM of porous silicon after anodization at $J_a = 150$ A/m^2 for 30 min.

3. Experimental

The substrates used for diamond deposition were 3-inch diameter ⟨100⟩, p-type, and 0.4–1 mm thick polished silicon wafers. Prior to dry seeding, the wafers were cleaned in a freshly prepared pirannah etch (H_2SO_4/H_2O_2 cleaning solution in the ratio of 7:3) followed by a quick etch in 10% HF solution. A small amount of diamond powder was dispensed on top of the wafer and the surface was polished thoroughly using clean lint free paper. Afterwards, the extra diamond powder was blown away using nitrogen gas. The diamond particle size used for polishing the silicon wafers was 4 nm.

Diamond films were deposited in a Wavemat microwave plasma disc reactor (MPDR). It uses a microwave power generator that operates at a frequency of 2.45 GHz, with a maximum power rating of 6 kW. Power and pressure were varied in the range of 2800–3300 W and 50–60 Torr, respectively, while the methane concentration was kept constant at 1%. The substrate temperature was maintained at around 850°C.

The anodizing cell used for anodization of silicon was made of Teflon. The electrolytic solution used to form the porous layer was $HF/H_2O/C_2H_5OH$ in the ratio of 1:1:2. The cathode was a platinum grid which was placed at a distance of 2 cm from the wafer. The silicon wafer acts as the anode. It was coated with silver paste on the backside for good electrical contact. A copper plate provided electrical contact and support on the backside of the wafer. The current density applied was in the range of 100–200 A/m^2. A digital multimeter was used to measure the current. The anodizing process was done for a period of 15–30 min to get a good porous silicon layer on the silicon wafer. The diamond films were deposited on seeded and unseeded porous silicon substrates under the same deposition conditions as given above.

Surface morphology and roughness were determined using a Hitachi S-2000 scanning electron microscope (SEM) and Digital Instruments atomic force microscope (AFM). A Philips Model X-pert system X-ray diffractometer was used for stress measurement and film texture analysis. This system uses a Cu Kα (wavelength $\lambda =$ 0.15406 nm) X-ray source operating at 45 kV and 40 mA. The residual stress in the films was measured using the same

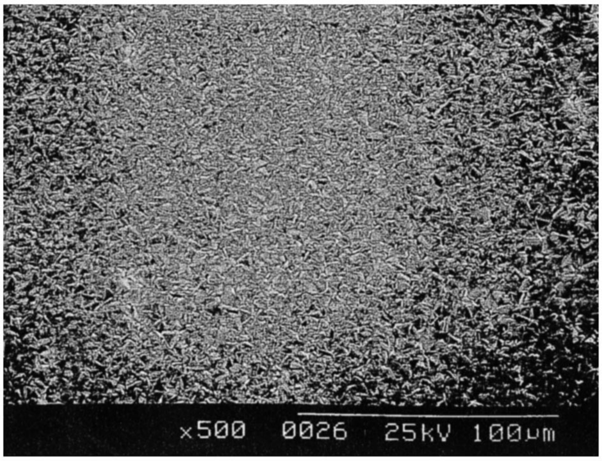

Fig. 3. SEM showing uniform diamond film growth in some regions on porous silicon substrate without dry seeding.

system by the $d\sin^2\psi$ technique, where d is the lattice spacing calculated using the Bragg law: $2d\sin\theta = n\lambda$, and ψ is the sample tilt [4]. For maximum sensitivity, Bragg reflection due to (331) planes was used; the corresponding 2θ being at around 140°.

4. Results and discussion

4.1. Anodization results

Fig. 1 shows an SEM picture of a sample anodized at a current density $J_a = 150$ A/m^2 for 15 min. The pore size is essentially the same for 100 A/m^2. The AFM results in Fig. 2 show that the average roughness is approximately 121 nm and the maximum depth of the layer is approximately 1 μm. A uniform porous layer was formed on the surface of the silicon substrate.

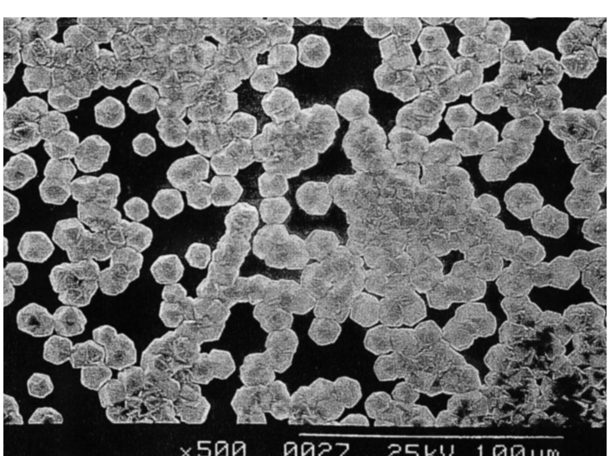

Fig. 4. SEM showing non-uniform diamond film growth in some regions on porous silicon substrate without dry seeding.

4.2. Deposition without dry seeding

Diamond was deposited onto porous silicon substrates prepared by anodizing silicon wafers. The substrates were dipped in HF prior to deposition to remove any oxide layer formed on top of the porous layer. The wafer was not subjected to any dry seeding before depositing the diamond. They were weighed before deposition. An SEM picture of a diamond film deposited on a porous silicon sample without being subjected to the dry seeding technique is shown in Fig. 3. Another SEM at the same magnification is shown in Fig. 4 for another region of the film. It shows that the diamond film is not uniform; it is continuous in some regions but discontinuous in others. The weight of the diamond film was approximately 40 mg. The film non-uniformity and discontinuity could be due to the fact that the porous layer did not have the desired uniformity and the pore size may have been too big. Nevertheless, this experiment proves that diamond grows on porous silicon without any assistance from a seeding/scratching technique. The problem of non-uniform diamond growth can be overcome by optimizing the pore size and the thickness of the porous layer.

4.3. Deposition with dry seeding

The porous silicon substrates were dry seeded with 4-nm diamond particles prior to deposition. The microwave power and pressure used was 3400 W and 58 Torr, respectively. The methane concentration was kept at 1%. The substrate temperature was approximately 830°C. The total deposition time was 20 h. The deposition rate was approximately 0.35 μm/h and the thickness of the diamond film was approximately 7 μm. The SEM results are shown in Fig. 5. The diamond film is continuous and uniform over the entire substrate. There were no obvious microcavities found in the film. However, at some places there is some clustering of diamond particles as shown in Fig. 6. This could be due to the size of the pores. The thickness of the porous layer and the size of the pores may be too large. There could also be clumps of diamond particles trapped in the pores which would cause the formation of large size diamond particles.

The stress measurement plots (distance, d, between (331) planes versus $\sin^2\psi$, where ψ is the sample tilt) for diamond films deposited on silicon substrates with and without anodization are shown in Fig. 7. Linear regression was used to fit a straight line through the experimental points and the stress was extracted from the slope as described in Ref. [4]. A compressive stress of about 500 MPa is expected in these films due to the CTE mismatch between diamond and silicon. Tensile stress is normally expected in deposited diamond films since abstraction of H from two neighboring C—H bonds yields a C—C diamond bond and H_2 is released. Such reactions normally yield tensile stress in a film [5]. The diamond film deposited on an unanodized dry seeded silicon substrate has a total (intrinsic and CTE related) compressive

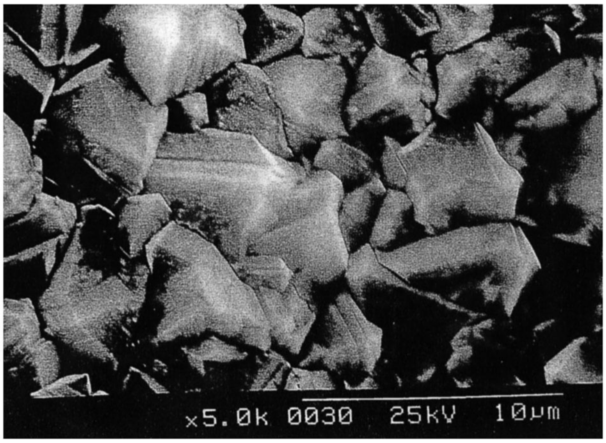

Fig. 5. SEM showing uniform diamond film growth on porous silicon substrate with dry seeding.

stress of 140 MPa. The total compressive stress present in the film deposited on an anodized silicon substrate is 440 MPa. This means that there is a net tensile stress of 360 MPa (after subtracting the CTE related stress component) in the diamond film deposited on an unanodized substrate, whereas, it is only 60 MPa in the case of a porous Si substrate. Therefore, it can be stated that porous silicon substrates result in diamond films with a significantly reduced stress. The stress reduction may be due the intermediate compliant porous layer, which relieves the net stress in the film.

The adhesion of the diamond film to the porous silicon substrate was measured and was found to be 11 MPa, whereas, the adhesion of diamond film to a plain silicon substrate is less than 7 MPa. This may be because of the increased surface area and a better interaction between the growing diamond and the surface silicon atoms in the case of porous silicon. Carbon atoms may also penetrate deep into the substrate, producing better adhesion. Hence, porous silicon not only produces a lower stress in diamond films, but also better adhesion.

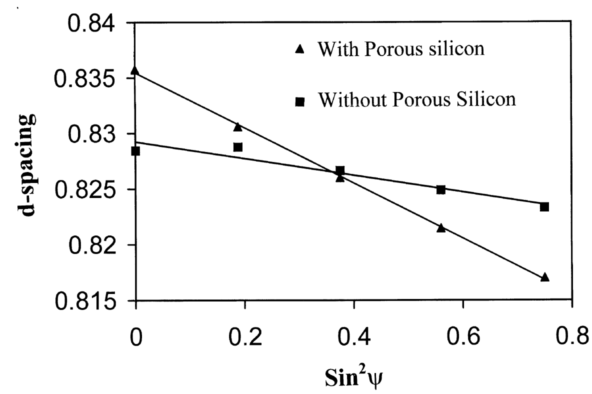

Fig. 7. Stress measurement plot (d vs. $\sin^2\psi$) of diamond film grown on dry seeded silicon with (solid triangles) and without (solid squares) porous Si layer.

To solve the problem of clustering of diamond particles, we changed the dry seeding procedure. Instead of dry seeding the porous silicon substrate by rubbing with diamond particles, we poured diamond powder onto the substrate and then softly wiped the excess powder away. Thus, a porous silicon substrate with diamond particles trapped in the pores was obtained. Diamond was deposited on this substrate for 20 hours. A uniform film was obtained without any discernible large clusters on the entire surface as seen by SEM. Fig. 8 shows an SEM picture of the resulting diamond film. This is typical of the entire surface. It is clear, thus, that by reducing the density of trapped diamond clusters in the pores, a uniform deposited layer of diamond could be obtained.

5. Conclusions

Diamond deposited on porous silicon without any dry

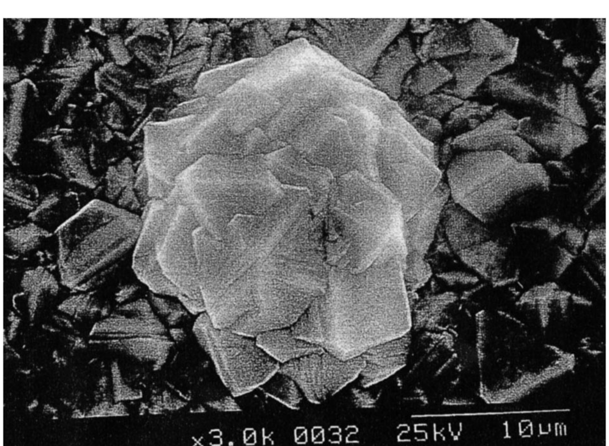

Fig. 6. SEM showing diamond cluster growth in some regions on porous silicon substrate with dry seeding.

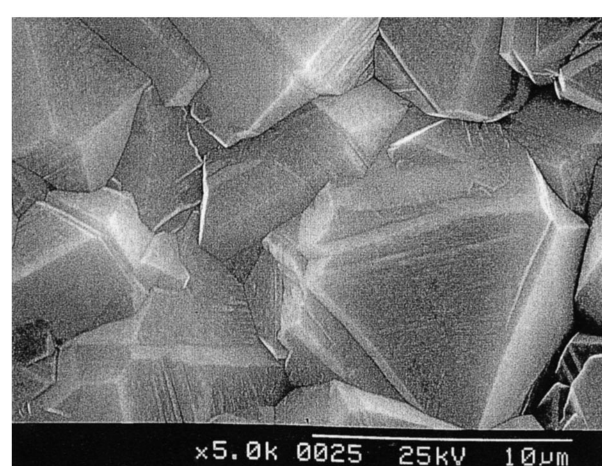

Fig. 8. SEM showing typical diamond morphology of films deposited on porous silicon with soft seed dispensing technique.

polishing gave non-uniform deposition and low deposition rate. Nevertheless, it was established that nano-deformities are potential diamond nucleation sites. Diamond films deposited on porous silicon dry seeded with 4 nm diamond powder gave uniform nucleation and high deposition rates. The porous silicon layer helped trap diamond nano-particles efficiently to enhance the nucleation density. Thus, nano-deformities and the diamond seed particles left on the substrate are extremely useful for obtaining high nucleation densities, as well a uniform growth. Porous silicon allowed the stress in deposited diamond films to be reduced considerably. The adhesion of diamond film to the substrate also improved with the use of a porous silicon layer.

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