Electrical characterization of CVD diamond thin films grown on silicon substrates

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Abstract

Diamond thin films grown on high resistivity, (100) oriented silicon substrates by the hot filament chemical vapor deposition (HFCVD) method have been characterized by four-point probe and current-voltage (through film) techniques. The resistivities of the as-grown, chemically etched and annealed samples lie in the range of $10^2$ to $10^6$ Ω cm. The Raman measurements on these samples indicate sp$^3$ bonding with a sharp peak at 1332 cm$^{-1}$. The surface morphology as determined by scanning electron microscope shows polycrystalline films with (100) or (111) faceted structures with average grain size of $\approx 2.5$ μm. The through film current-voltage characteristics obtained via indium contacts on these diamond films showed either rectifying or ohmic behavior. The difference in Schottky and ohmic behavior is explained on the basis of the high or low sheet resistivities measured by four-point probe technique. 5% methane to hydrogen concentration during film growth resulted in poor surface morphology, absence of sp$^3$ bonds, and low resistivity.

Keywords: Chemical vapour deposition; Diamond; Electrical properties and measurements; Silicon

1. Introduction

In recent years diamond has received considerable attention as a high temperature, high frequency and high power electronic device material [1]. The ability to deposit high quality diamond polycrystalline thin films on silicon substrates at reasonable temperatures and pressures by chemical vapor deposition (CVD) technique has led to the feasibility of economical device fabrication using inexpensive silicon substrates [2-4]. However, the electrical properties of polycrystalline diamond thin films show significant variations due to annealing in vacuum, oxygen or hydrogen and etching in chemical solutions [5-7]. The resistivities of as-deposited, undoped CVD diamond films are dependent on substrate surface preparation, film deposition technique and post deposition processing and thus vary from $10^2$ to $10^6$ Ω cm [8-10]. This significant variation of the resistivity is attributed to either hydrogen passivation of defect states or the presence of disordered graphitic regions between grains in the as-grown films. The resistivity is shown to increase by orders of magnitude after annealing the as-deposited films in nitrogen atmosphere to remove hydrogen from the films [6]. However, vacuum ($10^{-4}$ to $10^{-5}$ torr) annealing is found to reduce the film resistivity [9]. The graphitic regions on the surface can be chemically etched in a saturated solution of CrO$_3$ and H$_2$SO$_4$ at 170 °C. This chemical etching is also shown to increase the resistivity by a few orders of magnitude [8,9]. In this paper, an attempt is made to correlate through film current-voltage characteristics of the as-deposited and post deposition processed films to high and low sheet resistivities of thin films as determined by four-point probe technique. These high and low sheet resistivities are shown to be dependent on the methane to hydrogen ratio during film growth and post deposition processing.

2. Fabrication and processing

Several thin films of CVD diamond are fabricated in a hot filament CVD (HFCVD) system. The details of the CVD system are described elsewhere [11]. Table 1 gives details of the growth conditions of six different samples. The substrates were high resistivity ($>100$ kΩ cm), (100) oriented silicon substrates that were cleaned in acetone, etched in HF in an ultrasonic bath, scratched with diamond paste (1 or 9 μm particle size) and sonificated in the ultrasonic bath. Only for sample S3 the CH$_4$/H$_2$ ratio was 5.0%. Front contacts were formed by depositing indium dots (0.1 μm thick, 0.05 cm diameter) on the CVD diamond thin films in a thermal
Table 1
Growth conditions. As-deposited samples; thickness = 5-10 μm

<table>
<thead>
<tr>
<th>Sample</th>
<th>Run</th>
<th>Pressure (Torr)</th>
<th>CH₂/H₂ ratio (%)</th>
<th>Flow rate (sccm)</th>
<th>Substrate temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>31110</td>
<td>39.9</td>
<td>1.0</td>
<td>200</td>
<td>850</td>
</tr>
<tr>
<td>S2</td>
<td>31110</td>
<td>39.9</td>
<td>1.0</td>
<td>200</td>
<td>850</td>
</tr>
<tr>
<td>S3</td>
<td>40126</td>
<td>38.7</td>
<td>5.0</td>
<td>200</td>
<td>850</td>
</tr>
<tr>
<td>S4</td>
<td>31110</td>
<td>39.9</td>
<td>1.0</td>
<td>200</td>
<td>850</td>
</tr>
<tr>
<td>S5</td>
<td>31110</td>
<td>39.9</td>
<td>1.0</td>
<td>200</td>
<td>850</td>
</tr>
<tr>
<td>S6</td>
<td>31110</td>
<td>39.9</td>
<td>1.0</td>
<td>200</td>
<td>850</td>
</tr>
</tbody>
</table>

Post deposition processed samples: S1a: S1 annealed in vacuum (10⁻⁶ torr) at 600 °C for 15 min. S2a: S2 annealed in vacuum (10⁻⁶ torr) at 600 °C for 15 min. S4e: S4 etched in CrO₃ and H₂SO₄ at 170 °C for 60 min. S5e: S5 etched in CrO₃ and H₂SO₄ at 170 °C for 60 min. S6e: S6 etched in CrO₃ and H₂SO₄ at 170 °C for 60 min.

evaporation system. Back ohmic contacts were obtained by depositing 1 μm thick indium film on the entire backside of the silicon substrates.

3. Experimental results

3.1. Electrical properties

The electrical properties of the HFCVD diamond films were determined by two methods, i.e., four-point probe method and through film current-voltage (I-V) characteristics observed on a curve tracer. Fig. 1 shows a plot of through film I-V characteristics for four samples; S1a, S2a, S3 and S4e. Samples S1a and S3 show ohmic behaviour where as S2a and S4e show Schottky type behavior. Sample S2 turns on at about 3 V and does not breakdown until about 20 V are reached in the reverse direction. Sample S4 also turns on at about 3 V but current increases linearly (rather than exponentially) with increasing voltage in the forward direction. This sample breaks down around 10 V in the reverse direction. The results of the four-point probe measurement for the samples S1 to S6 are shown in Table 2. The resistivity of sample S1 decreased from $1.24 \times 10^5$ Ω cm for as-deposited sample to $8.53 \times 10^4$ Ω cm after annealing the sample in vacuum at 600 °C for 15 min. On the other hand, in sample S2 the resistivity increased slightly after annealing in vacuum at 600 °C for 15 min. In three samples, namely S4, S5 and S6 the resistivity increased by more than an order of magnitude after chemically etching the samples in a solution of CrO₃ and H₂SO₄ at 170 °C for 60 min.

3.2. Raman characteristics

The Raman spectra obtained by the ISA Jobin-Yvon U1000 spectrometer (uses 514.4 nm argon line) shown in Fig. 2(a) and Fig. 2(b) for samples S1 and S3 show dramatic differences. For sample S1 [Fig. 2(a)], a single sharp peak centered at 1330 cm⁻¹ with a full width at half-maximum (FWHM) of 7.0 cm⁻¹ is observed. The plot is indicative of the diamond phase (sp³ bonds) of the material. Samples S2 and S4 also show similar Raman spectra. Sample S3 shows two broad bands peaking approximately at 1350 cm⁻¹ and at 1560 cm⁻¹. This plot is indicative of amorphous carbon phase of the material [12]. It should be noted that the CH₂/H₂ ratio for S3 is 5.0% whereas that ratio is 1.0% for S1, S2 and S4.

3.3. SEM characteristics

A JEOL JSM-35 scanning electron microscope is used to observe the surface morphologies of the as-deposited and post deposition processed samples. Fig. 3(a) and Fig. 3(b) show SEM pictures of samples S1 and S1a, respectively. In spite
of a decrease of resistivity by two orders of magnitude, there is no significant variation in the surface morphology of the two samples. There appears to be an improvement in the faceted structure after annealing. Fig. 4(a) and Fig. 4(b) compare the surface morphologies of an as-deposited (S4) and a chemically etched sample (S4e). The beautiful faceted structure seen in Fig. 4(a) has somewhat disappeared after chemical etching. Lastly, an SEM photograph of sample S3 is shown in Fig. 5(a). The increase in methane concentration from 1.0% to 5.0% has led to a film with no microscopically visible crystallographic facets. Fig. 5(b) shows a cross-sectional view of sample S1, showing uniform growth. This SEM picture is used to estimate the thickness of the sample (≈ 6 μm). This thickness is used in the calculation of sheet resistivity.

4. Discussion

The dependence of the electrical properties, i.e., the resistivity and carrier concentration determined from Hall measurements and their dependence on sp³ bonding is described in a previous paper [13]. In this paper, we report the dependence of resistivity measured from a four-point probe and through film I-V characteristics on sp³ bonding and surface morphology of the films. Sample S3 is a very low resistive ($p = 2.21 \times 10^7 \Omega \text{ cm}$) film simply because it is grown with a 5.0% methane to hydrogen concentration. Its Raman spectra indicates amorphous carbon film and the SEM picture shows...
a very poor quality film. The through film I-V characteristics of this as-deposited sample shows almost a linear curve suggesting good ohmic contact formation. Indium contacts to graphite or hydrogenated amorphous carbon films are shown to result in good ohmic contacts as indicated by the sample S3 here [14]. Samples S1, S2 and S4 though prepared under identical conditions in the same run yield very different through film I-V curves after post deposition processing (see Fig. 1). Surface sheet resistivity of these as-deposited samples varied from 1.66 × 10⁴ Ω cm to 1.24 × 10⁵ Ω cm. This small variation in resistivity is mostly due to slightly different hydrogen content in the film, based on the location of the sample during fabrication [15].

The Raman spectra and the SEM photographs of S1, S2 and S4 show very similar results and the reasons for small variations in resistivity cannot be ascertained either by Raman spectra or surface morphology. The Schottky and ohmic contact formation to diamond thin films is not very well understood [16]. Indium contacts to low resistivity (heavily doped) GaAs samples lead to good ohmic contact formation [17] and the same indium contacts to high resistivity (low doped) GaAs samples lead to Schottky contact formation [18]. The diamond thin film samples though not intentionally doped show significant variations in resistivity similar to doped GaAs samples. A change from Schottky type contact to ohmic contact depending on the doping concentration is due to the change of transport mechanism from thermionic emission to thermionic field emission or field emission [19]. This trend is also observed in our experimental results of indium contacts to diamond. Sample S1a and S3 which show ohmic behavior have very low sheet resistivities i.e., ρS1a = 8.53 × 10⁴ Ω cm and ρS3 = 2.21 × 10⁴ Ω cm. Samples S2a and S4e show Schottky behavior because of high sheet resistivities of these samples i.e., ρS2a = 1.09 × 10⁵ Ω cm and ρS4e = 7.90 × 10⁵ Ω cm. Thus, it appears that formation of Schottky and ohmic contacts to diamond may be controlled by appropriate processing (annealing or chemical etching) or by changing methane to hydrogen ratio during deposition. However, the stability of these contacts at high temperature operation needs to be checked. Although we have observed decrease of sheet resistivity after annealing in vacuum at 600 °C in a few samples, it is not clear whether this is caused by conversion to graphitic phase. Chemical etching has always yielded higher resistivities showing clearly that the surface of diamond films have either graphitic regions or a high concentration of hydrogen. The highest sheet resistivity obtained here is 2.60 × 10⁸ Ω cm.

5. Conclusion

The through film current-voltage characteristics of CVD grown diamond thin films on silicon substrates show either Schottky or ohmic behavior depending upon the sheet resistivity of the sample measured by four-point probe technique. The sheet resistivity of CVD diamond films is shown to be dependent on methane to hydrogen ratio used during film growth, vacuum annealing or chemical etching. Increasing methane to hydrogen ratio from 1.0% to 5.0% resulted in low sheet resistivity. However, the quality of the material is extremely poor as evidenced by Raman spectroscopy and very poor surface morphology as observed in a scanning electron microscope. Vacuum annealing at 600 °C for 15 min also yielded low sheet resistivities in two samples but in the third sample resistivity increased. No significant variations were observed either in Raman spectra or in surface morphology after chemical etching of the samples. No significant variations in the surface morphology were observed after vacuum annealing. Thus the changes observed in sheet resistivities due to post deposition processing cannot be correlated to the bond structure (sp³ vs. sp²) or surface morphology at present time.

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References