LOW TEMPERATURE GROWTH OF ULTRANANOCRYSTALLINE DIAMOND ON GLASS SUBSTRATES FOR FIELD EMISSION APPLICATIONS*

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ABSTRACT

Recent studies of field emission from diamond have focused on the feasibility of growing diamond films on glass substrates, which are the preferred choice for cost-effective, large area flat panel displays. However, diamond growth on glass requires temperatures $\leq 500^\circ\text{C}$, which is much lower than the temperature needed for growing conventional microwave plasma chemical vapor deposition (CVD) diamond films. In addition, it is desirable to minimize the deposition time for cost-effective processing. We have grown ultrananocrystalline diamond (UNCD) films using a unique microwave plasma technique that involves CH_4 -Ar gas mixtures, as opposed to the conventional CH_4 - H_2 plasma CVD method. The growth species in the CH_4 -Ar CVD method are C_2 dimers, resulting in lower activation energies and consequently the ability to grow diamond at lower temperatures than conventional CVD diamond processes. For the work discussed here, the UNCD films were grown with plasma-enhanced chemical vapor deposition (PECVD) at low temperatures on glass substrates coated with Ti thin films. The turn-on field was as low as $3\text{ V}/\mu\text{m}$ for a film grown at 500°C with a gas chemistry of $1\%\text{CH}_4/99\%\text{Ar}$ at 100 Torr, and $7\text{ V}/\mu\text{m}$ for a film grown at 350°C . UV Raman spectroscopy revealed the presence of high quality diamond in the films.

INTRODUCTION

Diamond thin films and related materials are being extensively investigated because their low threshold field electron emission properties make them desirable for use in cold cathode-based devices. Work has been done on diamond-coated Si and Mo tips,^{1,2,3} flat diamond films,^{4,5,6} and other structures for use in field emission displays (FEDs). Most manufacturers of FEDs use glass substrates to minimize fabrication costs and because of their scalability to large area displays. In addition, most FEDs are currently fabricated using field emission arrays (FEAs) consisting of field emitter tips (i.e., sharp Mo or Si conical features) located at the center of a hole in a metallic layer (gate) above the tips. A major problem with current FEA technology is that the threshold field for emission is relatively high, and the surface of the tips are susceptible to contamination, leading to emission instability, and in some cases to runaway discharges that can destroy large portions of the array. In addition, the fabrication of field emitter tips generally requires several high precision alignment steps, resulting in added cost. Therefore, it is desirable to develop FEAs on glass substrates based on flat field emitters with low threshold field and stable and uniform electron emission.

Conventional microwave plasma chemical vapor deposition (CVD) of diamond involves CH_4 as a precursor in a large background of hydrogen. These films are typically grown at 800 - 1000°C , which melts most glasses of interest for use in FEDs. At lower temperatures, the conventionally grown diamond has a very low growth rate and it can take up to 20 hours or longer to form a continuous film.

Previous studies of low temperature growth of UNCD films on Si substrates, using an Ar/ CH_4 microwave plasma, indicated that the films grow with an activation energy of 5.85 kcal/mol .⁷ This is in agreement with the activation energy calculated from first principles theory for growth based on carbon dimer insertion directly into the diamond lattice.⁸⁻¹⁰ Conventional microwave CVD using CH_4/H_2 plasmas has typical activation energies in the range of 20 - 30 kcal/mol . In our CVD system, if one uses a substrate temperature of 800°C and a $1\%\text{CH}_4/99\%\text{H}_2$ gas pressure of 100 Torr, we find a growth rate of $\sim 1\text{ }\mu\text{m/hr}$ for conventional

microcrystalline (MCD) films, vs $\sim 0.25 \mu\text{m/hr}$ for the UNCD films grown with 1% CH_4 / 99% Ar. Using these growth rates at 800°C , the experimentally measured activation energy of 5.85 kcal/mol for UNCD, and an assumed activation energy value of 24 kcal/mol for the MCD films, an Arrhenius plot can be constructed as shown in Figure 1. This plot shows that the UNCD has a higher anticipated growth rate than MCD in the temperature regime below $\sim 650^\circ\text{C}$. According to this calculation, the growth rate of the UNCD film is ~ 100 times that of MCD at 350°C . In practice, we were unable to obtain measurable growth of continuous MCD films or to verify that the deposits were diamond using a $\text{CH}_4\text{-H}_2$ plasma at substrate temperatures below $\sim 500^\circ\text{C}$.

FIG. 1. Plot of the calculated growth rates vs reciprocal substrate temperature for UNCD and MCD films, using literature values for the activation energies.

EXPERIMENTAL

The UNCD films were grown on quartz glass slides coated with Ti layers (thickness: 200 nm) produced by magnetron-sputter deposition. A diamond nucleation layer was formed using an ultrasonic bath with a suspension of diamond powder (0.1 micron particle size) for ten minutes. The films in this study were grown using an ASTeX PDS-17 2.45 GHz microwave plasma deposition system with 3.5 kw rf induction substrate heater. The process gas used was a 1% CH_4 and 99% Ar mixture, with a total flow of 100 sccm. The growth took place at a total power of 600 Watts and a pressure of 100 Torr. We grew films at various substrate temperatures from 350°C to 500°C . The UNCD films were characterized using UV Raman spectroscopy at 266 nm wavelength. The electron emission properties of the films were characterized using a computer-controlled current vs. voltage measurement system⁶ involving an anode-cathode nominal gap of 50 μm .

RESULTS AND DISCUSSION

Figure 2 shows the UV Raman spectrum of UNCD films grown on Ti-coated quartz at substrate temperatures of 350 and 500°C . The intensity of the 1332 cm^{-1} peak can be correlated with the sp^3 bond content in the films, and is indicative of their highly crystalline nature. This is confirmed by the low intensity of the peak at 1580 cm^{-1} , corresponding to a very low sp^2 bond content in the films. The Raman spectra indicate that there is very little degradation of the

crystalline quality of the diamond films even at temperatures as low as 350 °C. In this case, the UNCD films were grown with no additional heating applied via the substrate heater, and because of the plasma-induced surface heating, 350 °C was the lowest achievable temperature. It should be noted that the film grown at 500 °C is approximately twice as thick as the film grown at 350 °C (120 nm vs. 60 nm), and that the sp^2/sp^3 ratio is similar for the two films. The UV Raman data shown in Figure 2 are very similar to those obtained for films grown using the same plasma parameters at substrate temperatures of 800 °C, which have been demonstrated to be phase-pure diamond by a variety of experimental method^{3,6-9}. Additional work using TEM will be carried out to further characterize the morphological properties of these low-temperature films.

FIG. 2. UV Raman Spectroscopy of the UNCD films grown at 350°C and 500°C, showing the sharp sp^3 bonding at 1332 cm^{-1} indicating the presence of diamond.

The low-temperature UNCD films on Ti/quartz substrates exhibit excellent field emission properties, as shown in Figure 3. The onset field is as low as 3 V/ μm for a film grown at 500 °C, and the average across the film is 5-8 V/ μm . It should be noted that these films require no pre-

FIG. 3. Field emission of the film grown at 500°C. Data represents an average of 5 cycles of increasing and 5 cycles of decreasing voltage.

FIG. 4. Field required to retain a constant current of 0.1 μA and 5 μA , showing the uniformity of the field emission across a 1 cm^2 sample.

conditioning of the surface, exhibit little hysteresis between increasing and decreasing voltage cycles, and have a first-time turn-on behavior that is the same as succeeding measurements. The film grown at 350 °C exhibits uniform emission across a 1 cm² area with onset fields in the 7-9 V/μm range. Figure 4 shows the spatial uniformity of field emission for a film grown at 350 °C. The figure displays the fields required to obtain constant currents of 0.1 μA and 5 μA. The field required for 5 μA emission current varies less than 3 V/μm across the entire 1 cm² film. Measurement of the emission site density requires the use of a phosphor screen to image the entire emitting surface. This experiment is in preparation.

CONCLUSIONS

We have grown UNCD thin films on glass substrates at temperatures as low as 350 °C. UV Raman analysis revealed that films grown at low substrate temperatures, using the same plasma parameters previously utilized in our laboratory for synthesizing high temperature phase-pure nanocrystalline diamond films, also have a high sp³ vs sp² relative content. These low temperature UNCD films exhibit threshold fields as low as 3 V/μm for a film grown at 500 °C, and 7 V/μm for films grown at 350 °C, with uniform field emission across a 1 cm² sample. These results indicate that UNCD films can be integrated with glass substrates for fabrication of field emission displays and other cold cathode-based devices requiring cost-effective substrates.

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