# Field emission of diamond films grown on glass substrates at low temperatures

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Abstract − Using microwave plasma-enhanced chemical vapor deposition, diamond films were successfully grown on Ti-coated glass substrates at temperatures as low as around 500°C in behalf of practical applications to field emitters. Electron emission was observed at turn-on fields below 18 V/μm. Field emission characteristics of diamond films were discussed in terms of their crystalline qualities. Diamond films with poorer crystalline qualities showed better field emission properties.

## I. Introduction

Diamond films have attracted much attention as one of promising candidates for field emitters due to their superior properties such as chemical inertness, thermal stability, negative electron affinity, resultant low turn-on voltages, and immunity to sputtering [1]. Field emission displays, whose emitters are the target application of diamond films in this study, in most cases, are fabricated using glass substrates for the purpose of low cost and easy processing. Glass substrates are 10 times cheaper than silicon wafers and are of great advantage in vacuum sealing. For practical applications, therefore, diamond films are recommended to be deposited on glass substrates, which requires diamond growth below 600°C to prevent glass substrates from softening. In most cases, however, temperatures for diamond growth in a microwave plasma-enhanced chemical vapor deposition (MPECVD) system are around 800°C such that the deposition temperatures should be lowered at least by 200°C to meet the temperature requirement for the growth on glass substrates. It has been well known that the lower the deposition temperatures are, the more probably the non-diamond phases occur [2]. There are two main ways in decreasing the growth temperatures of diamond films in MPECVD [3]. One is to use carbon-oxygen gas mixtures and the other is to decrease plasma densities by reducing microwave powers or cham-

ber pressures. With oxygen species added to the plasma, diamond films can be deposited at lower temperatures, which results from effectiveness of oxygen species in etching the non-diamond phases. For the oxygen-containing plasma, however, a decrease of the deposition temperatures is traded off with a reduction of the deposition rates due to high etching rates. The effect of the microwave powers and pressures on the growth temperatures is able to be understood straightforwardly. Besides the issue of the glass substrates for the practical applications, the low temperature growth seems to be beneficial even to the field emission characteristics of diamond films. This is because diamond films grown at lower temperatures retain poorer crystalline quality, which in turn show better field emission properties [4].

This study investigates the low temperature growth of diamond films on Ti-coated glass substrates by changing deposition parameters of MPECVD such as microwave powers, agitation time, particle sizes of diamond powder for agitation, and methane concentrations. The field emission characteristics of diamond films were discussed with correlation to their microstructures and film qualities.

## II. Experimental

An MPECVD system (ASTeX, 2.45 GHz, 1.5 kW) was used to deposit diamond films on Ti-coated

glass substrates, as described in detail elsewhere [4]. Prior to the deposition, glass plates were softly scratched with SiC papers (#1200) to improve the adhesion between glass substrates and Ti films. Ti films were coated on the glass plates using DC magnetron sputtering, followed by agitation with diamond powders in distilled water, rinsing in acetone, ethanol, and distilled water, and then blowing with nitrogen gas.

Deposition parameters of diamond films were engineered in terms of growth temperatures, film adhesion, and growth rates. Diamond films were grown on the following conditions: microwave power 500-700 Watt, pressure 20 Torr, $CH_4$ concentration 2% in the growth step. The substrates were heated only by microwave plasma, and resultant temperatures were around 500°C. Prior to the growth step, the nucleation step was employed to increase the growth rates and the adhesion of films deposited at lower temperatures. When the methane concentration was high in the nucleation step, the diamond films were delaminated after the deposition was completed. In this experiment, the optimal methane concentration during the nucleation step was 4% for the good film adhesion and proper growth rates. Detailed deposition conditions are listed in Table 1.

As-grown diamond films were characterized using micro-Raman spectroscopy (Renishaw 3000) with the 514.5 nm line (2.41 eV) of an Ar ion laser, atomic force microscopy (AFM, PSI LS), scanning electron microscopy (SEM), and X-ray diffraction spectroscopy (XRD). Field emission properties were measured in a diode mode under a vacuum of $10^{-7}$ to $10^{-8}$ Torr. More details on the measurements may be found in our previous report [4].

## III. Results and Discussion

Raman spectra of the diamond films are given in Fig. 1 (a). The spectrum of the sample LT21 is decomposed by applying Lorentzian fits, as shown in Fig. 1 (b). The 1240, 1335, 1480, and 1640 $cm^{-1}$ peaks are characteristic of nanocrystalline diamond, polycrystalline diamond, amorphous carbon, and glassy carbon, respectively [4]. Fig. 1 (c), (d), and (e) show the decomposed peaks of LT36 at 1179, 1325, 1399, and 1508 $cm^{-1}$, of LT38 at 1240, 1328, 1411, and 1512 $cm^{-1}$, and 1240, 1332, 1420, and 1523 $cm^{-1}$, respectively. The crystalline qualities of diamond films are usually assessed by full widths at half maximum (FWHM) of the diamond peaks as well as ratios of the diamond peaks to the other non-diamond carbon peaks. The FWHMs of polycrystalline diamond peaks are 136, 68, 49, and 17 for LT21, L34, LT36, and LT38 respectively. On the other hand, the diamond peaks are relatively lower compared to the other non-diamond carbon peaks in the order of LT21, LT34, LT36, and LT38. Based on these measurements, the samples LT36 and LT38 possess higher crystalline qualities of diamond than LT21 and LT34, although the growth temperatures are lower for LT36 and LT38. However, the amounts of the diamond phase are smaller in the order of LT21, LT34, LT36, and LT38. Lower deposition temperatures generally cause lower crystallinity of diamond films and higher contents of non-diamond phases. With decreasing the growth temperatures, in this study, the crystalline qualities of diamond are higher, but the diamond phase increases in amounts, as shown in the FWHMs and the relative peak intensities of diamond, respectively. Only taking the growth temper-

**Table 1.** Deposition conditions of diamond films using MPECVD

| Samples | Temp (°C) | Agitation Time | Diamond powder sizes (μm) | Deposition time (hr.) | Nucleation step process |
|---|---|---|---|---|---|
| LT21 | 560 | 15 min | 30 | 63 | |
| LT26* | 560 | 15 min | 30 | 7 | |
| LT34 | 540 | 3 hour | 0.5 | 34 | $CH_4$ 8%, 1hr |
| LT36 | 540 | 5 hour | 0.5 | 60 | $CH_4$ 4%, 2hr |
| LT38** | 500 | 5 hour | 0.5 | 138 | $CH_4$ 4%, 2hr |

*Sample LT26 was treated with 0.25 μm diamond powder spray.
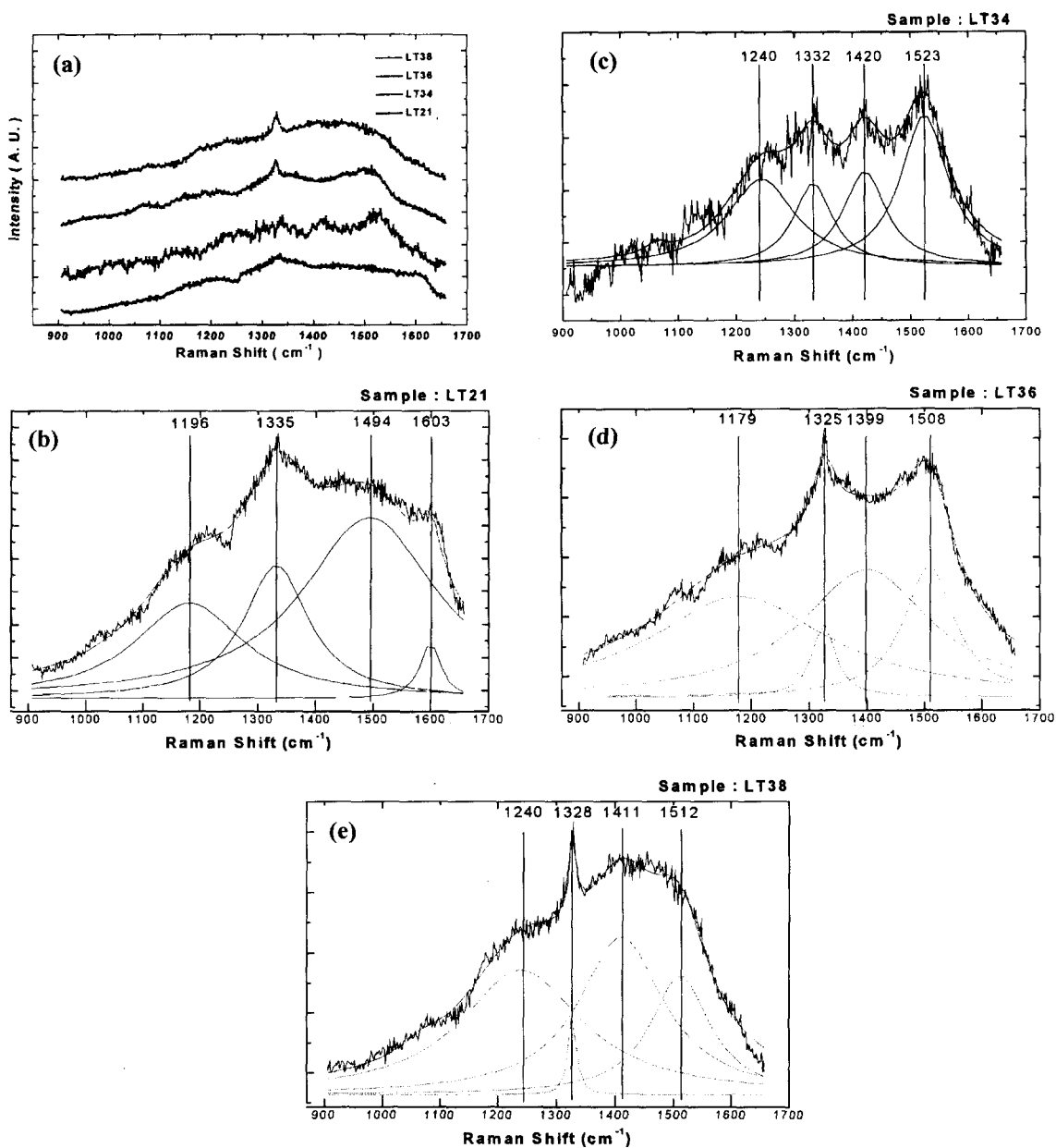**Sample LT38 was not fully covered.

**Fig. 1.** (a) Raman spectra of diamond films and their decomposed spectra of samples (b) LT21, (c) LT34, (d) LT36, and (e) LT38.

atures into account, it is not well explained why the higher film qualities are resulted at the lower temperatures. Therefore, this result seems to be ascribed to different nucleation steps, longer agitation time, and smaller particle sizes of diamond powders used for pre-treatment. From the diamond peak shifts, the

film stresses between diamond films and substrates of LT36 and LT38 are higher than that of LT21 [6]. It appears that the larger defect density along grain boundaries in the diamond film of LT21 diminishes the film stress.

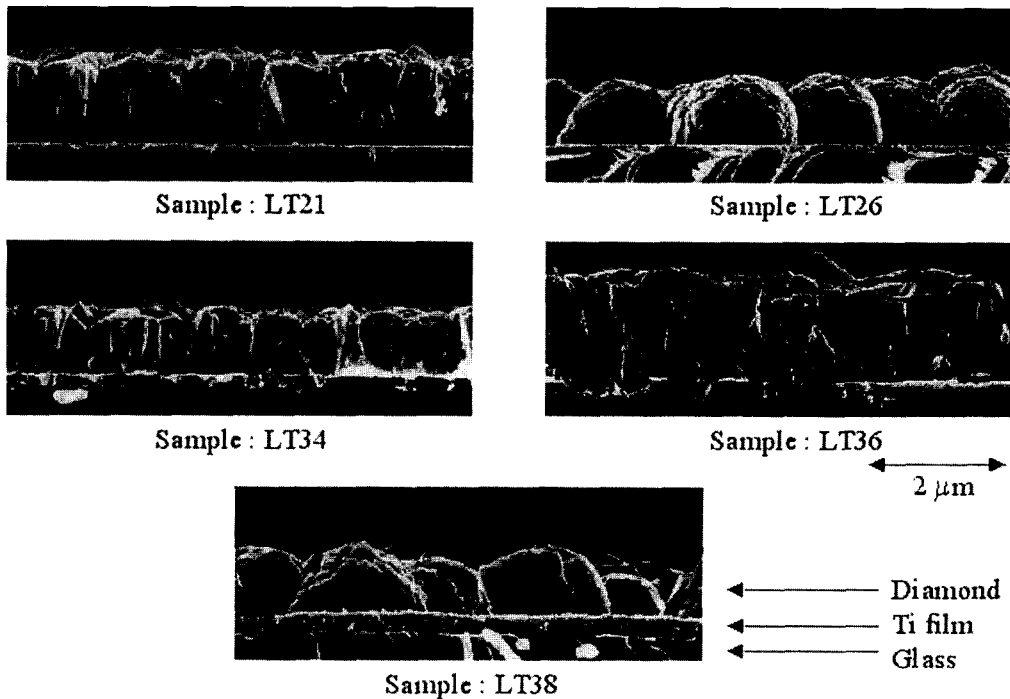Fig. 2 represents cross-sectional SEM images of

Fig. 2. Cross-sectional SEM images of diamond films LT21, LT26, LT34, LT36, and LT38.

as-deposited diamond films. All diamond films have the thickness of about 1.2 μm. LT21 and LT26 show different morphologies even though they were grown for 63 hr and 7 hr at the same deposition parameters but pre-treated at different conditions prior to diamond growth. Growth rate of LT26 is almost 9 times faster than that of LT21. The reason why LT26 shows the higher growth rate is that more diamond nucleation sites were provided because the diamond powder suspension (DP-Spray, P, Made in Denmark by Struers A/S) with 0.25 μm diameter was sprayed on LT26. Consequently, LT26 has the higher growth rate, poorer crystalline quality, and worse adhesion between the diamond and Ti films. The other samples, which were sonicated using diamond powders, shows denser and more facetted morphologies. The higher growth rates of LT34 and LT36 deposited at 540°C than that of LT21 grown at 560°C seems to result from the longer agitation time of diamond powders even at the lower deposition temperature. The film LT38 was not fully covered even for an extended deposition time, due to the low growth temperature of 500°C.

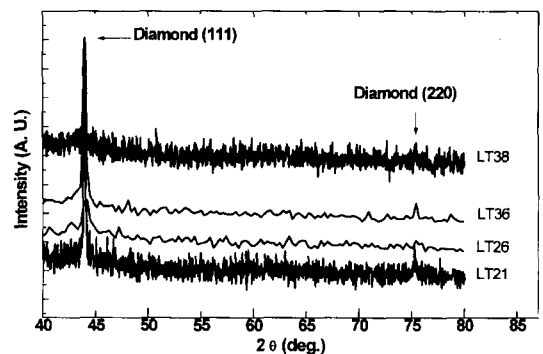The XRD spectra were taken to confirm the exist-



Fig. 3. X-ray diffraction spectra of diamond films LT21, LT26, LT, 36, and LT38.

ence of diamond phase and given in Fig. 3. The samples LT21, LT26, LT36, and LT38 show 2θ peaks at 43.92° and 75.3° that represent the diamond (111) plane and the diamond (220) plane, respectively. It is implied that the diamond films investigated are polycrystalline. The diamond phase was already confirmed to exist in the as grown films with Raman spectra and SEM observations.

Figs. 4, 5, and 6 show emission current densities measured against applied electric fields of the films
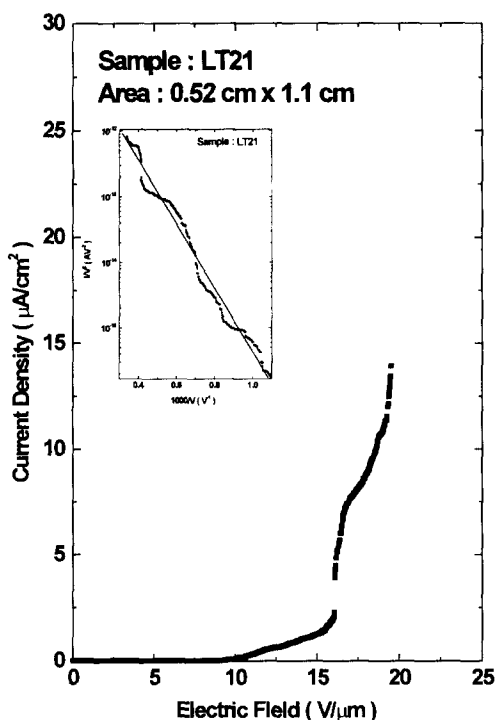
**Fig. 4.** Current density vs. electric field of the diamond film LT21, where its Fowler-Nordheim plot is given in the inset.
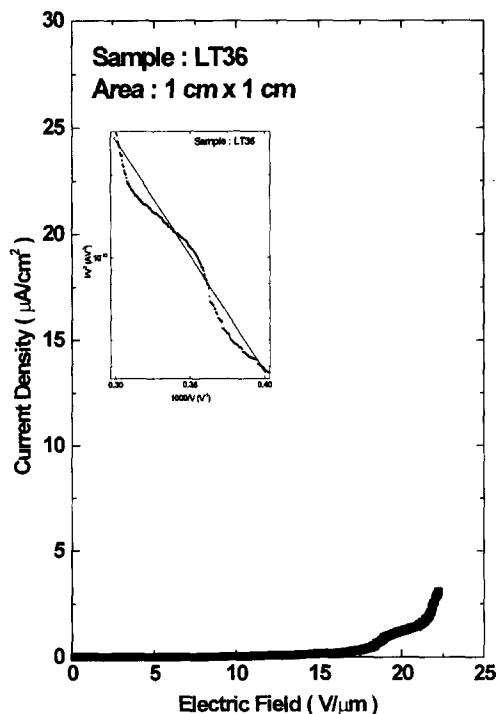


**Fig. 5.** Current density vs. electric field of the diamond film LT36, where its Fowler-Nordheim plot is given in the inset.

LT21, LT36, and LT38, where the insets give their Fowler-Nordheim plots. The current densities increase exponentially with the electric fields. The Fowler-Nordheim plots fits roughly to linear curves, indicating the field emission of electrons. More exactly, however, the Fowler-Nordheim plots are of meandering linear shapes. It seems that a deviation of the Fowler-Nordheim plots from the linearity is attributed to the involvement of several emission sources. Emission sites on the diamond film surfaces might move back and forth with increasing applied voltages. Slopes of the Fowler-Nordheim plots would fluctuate with the occurrence and disappearance of emission sites. A linear Fowler-Nordheim plot is expected in case of uniform emission over a large area. LT21 shows the turn-on field (defined as the electric field at which a current density is greater than 1 $\mu A/cm^2$) of 12 V/$\mu$m. Turn-on fields of LT36 and LT38 are 18 V/cm. LT21 gives a lower turn-on field than LT36 and LT38. As shown in Fig. 1, LT21 is of poorer crystalline quality than LT36 and

LT38. This result agrees well with the fact that diamond films with the lower crystalline quality possess better field emission characteristics [4]. Besides the film crystallinity, the surface roughness is another factor in affecting the field emission characteristics. This effect is figured out by measuring surface roughness of the diamond films over the area of 30 $\mu$m $\times$ 30 $\mu$m using AFM. The surface roughness is shown in Table 2. In comparison between the turn-on fields and the surface roughness, any concrete relationship can not be found such that the effect of surface roughness is negligible. Therefore, the crystalline qualities of films seem to be the major factor in determining their field emission properties. The electron emission mechanism can be understood in terms of an electron transfer to the film surfaces [7]. Electrons should move to the diamond film surface to be ejected. However, the diamond itself is an insulating material such that free electrons do not exist inside the diamond bulk. When non-diamond carbon phases coexist with the
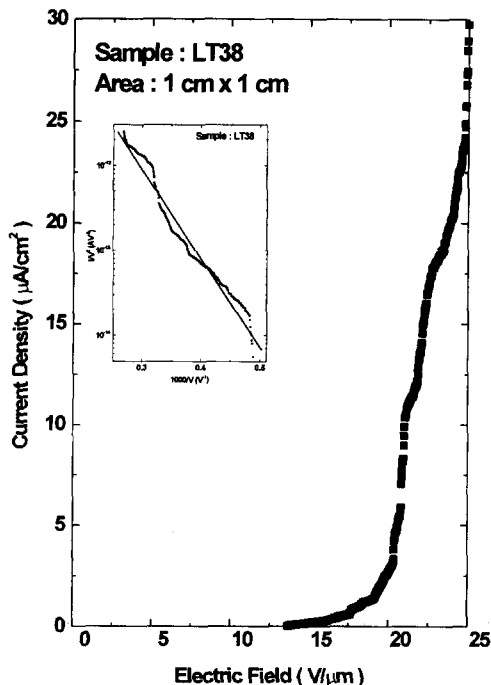
**Fig. 6.** Current density vs. electric field of the diamond film LT38, where its Fowler-Nordheim plot is given in the inset.

**Table 2.** Surface roughness measurements of diamond films using AFM

| Samples | rms Roughness (μm) |
|---------|--------------------|
| LT21 | 0.814 |
| LT26 | 0.627 |
| LT34 | 0.581 |
| LT36 | 0.945 |
| LT38* | not fully covered |

* Sample LT38 can not be measured.

diamond phase, electrons supplied from the electrode could be transferred to the film surface through these conductive paths. From this point of view, it is understandable that the LT21 with the poorer crystalline quality reveals a lower turn-on field than the LT36 and LT38.

## IV. Conclusion

Diamond films were successfully deposited on glass substrates at temperatures as low as around 500°C using MPECVD and their field emission characteristics were investigated. Decreasing the microwave powers led to the deposition of diamond films at lower temperatures and the growth rates of the diamond films were increased by engaging two step deposition, nucleation and growth steps. Growth temperatures were lowered down to approximately 500°C while keeping proper growth rates. The diamond films grown at low temperatures possess the turn-on fields lower than 18 V/μm. The field emission characteristics were interpreted in correlation with the crystalline qualities and surface morphologies of diamond films which were studied using Raman spectroscopy, XRD, SEM, and AFM. The diamond films with worse crystalline qualities show lower turn-on fields for electron emission. It seems that the crystalline quality of diamond films is the major factor in controlling field emission properties.

## Acknowledgement

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