Grain size influence on admittance of diamond thin films

M. C. Feliciangeli, M. C. Rossi, G. Conte
Electronic Engineering Dept and CNISM
University of Rome “Roma Tre”
Via della Vasca Navale, 84 – Rome, Italy

E-mail: gconte@uniroma3.it

Abstract. Small amplitude AC characterization of diamond thin films of different thickness and grain size has been carried out. The frequency dependent admittance, measured as a function of temperature, has evidenced similar trends for samples grown by using different deposition techniques, even if peculiar relaxations processes were found at higher temperatures in diamond films with larger grain sizes: changes in relaxation times activation energies related to grain sizes were observed. An analysis of imaginary impedance and electric modulus spectra enabled grain boundary, bulk and any other phase contribution to be separated and identified by reference to an equivalent electric circuit with three Voigt elements. Dielectric relaxations were studied concerning behavior of real permittivity.

1. Introduction
Polycrystalline diamond deposited by chemical vapor deposition (CVD) techniques is a wide gap semiconductor, and its potentialities have been recently demonstrated through the fabrication of surface channel MESFETs with transition frequencies of several GHz [1]. It has also been evidenced that MESFETs fabricated on hydrogen-implanted polycrystalline diamond thin films function at lower frequencies and work with the same operative mechanism [2]. Besides, channel conductance of devices fabricated on small grained surfaces crucially depends on hydrogenation recipes. It has also been observed that plasma hydrogenation time is longer in sp²-bonded carbon rich surfaces, probably due to an initial ablation by hydrogen radicals of such non-diamond carbon phases at grain boundaries (GBs) [3].

Polycrystalline diamond thick films are commonly thought as composed of diamond grains strongly oriented in the growth direction. Grain size increases from the nucleation side to the growth side and it is reasonable to consider that larger grains induce a decrease of GB phase in the film. It has been hypothesized [4] that DC charge transport mainly happens along percolating GBs, whereas the same transport mechanism is found in AC measurements performed with small amplitude signals, at least at low frequencies and temperatures [5-7]. Furthermore, it has been found that the combination of small grains and non-diamond carbon phases induces a grow-up of the dielectric permittivity, higher loss tangents and higher admittance and improves leakage currents compared to analogous large grained diamond films [8].

In order to better understand the role of grain surface and GBs on charge transport mechanisms by varying the grain size, eventually addressing limitations in electronic performances mainly linked to grain surface morphology, we characterized the AC response of two polycrystalline diamond films to

---

1 Contact author: gconte@uniroma3.it; Ph:+39-06-5517.7268, Fax:+39-06-5579.078

© 2008 IOP Publishing Ltd
small amplitude electric stimuli. Samples grown by hot filament (HF) and microwave (MW) assisted CVD technique were used. Frequency dependent admittance was measured as a function of temperature in the 1 mHz - 10 MHz range.

2. Experimental

Polycrystalline diamond films were deposited at high temperature starting from methane and hydrogen on electronic quality silicon substrates. The first sample studied, grown by HFCVD and named 24C2-62, was 62 μm thick, while the second one, named Ka8-105, was 105 μm thick and was deposited by MWCVD in presence of oxygen under optimized and selected conditions for this study. Addition of oxygen to the gas mixture permits, on one side, to rise the methane percentage increasing the growth rates and, on the other, takes away weakly bonded carbon atoms potentially leading to non-diamond phases. Morphology and structure of samples fabricated under the same deposition conditions of specimen 24C2 showed a preferred orientation along the <110> direction and line-shape analysis performed on the (220) reflection indicates a distribution of crystallite size (i.e. coherence distance) with average dimension around 41 nm [9]. Samples deposited under the same conditions as the Ka8 specimen showed a distribution with average grain size around 150 nm with a stronger <110> preferred orientation. More information about samples preparation can be found in [10,11]. Freestanding diamond films were obtained by etching away the silicon substrate in HF+HNO₃ acid solution. Dual side contacts were made on the top and bottom faces of freestanding samples by thermal evaporation of Silver. Dots of different radii (0.75–2.5 mm) were realized through a shadow mask in order to study the electrical properties in metal-diamond-metal vertical configuration. Measurements were implemented attaching samples bottom contact on a metal covered glass sheet with silver paste.

AC measurements were carried out by using a Solartron 1250 frequency response analyzer, equipped with a 1296 dielectric interface, and a HP4192A low frequency impedance bridge. A sinusoidal test voltage, equal to 1 Vpp without DC bias, was used at each frequency. Measurements were done under vacuum at each programmed temperature in the range 300–625 K with an accuracy of ±1K.

3. Results and discussion

Admittance formalism is mainly used for conducting materials because it emphasizes bulk properties as well as GBs transport. We model the probed heterogeneous material, constituted by grains and grain boundaries (GBs), as the equivalent of a frequency dependent conductance, $G(v)$, in parallel with a frequency dependent $C(v)$, representing the capacitance at a certain frequency. Admittance can then be written:

$$Y^* (v, T) = G_p (v, T) + j \omega C_{Tot} (v, T)$$

$G_p$ is the parallel conductance and $C_{Tot} = \varepsilon_0 \varepsilon_r A/d$ the probed material capacitance with the free space contribution $C_0 = \varepsilon_0 A/d$. In the last expressions $A/d$ is a geometric ratio, $\varepsilon_r$ the relative dielectric constant and $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m the vacuum permittivity. If we consider diamond grains and GBs as separated domains in parallel within the electric contacts, the total conductance and capacitance will be influenced at each frequency by the less resistive and most capacitive contribution, respectively. Figure 1 displays the frequency dependent conductance of sample Ka8-105.

Spectra show at least four different regimes of conductance. At each temperature an increasing trend with frequency is found, while an apparent saturation of conductance, which marks the onset of a vibrational regime (slope +1) is observed at higher frequencies. Increasing temperature, the general trend preserves: it only shows a rise of the low-frequency conductance. In order to identify and discuss different regimes found, we must compare this plot with more common spectra like those of sample 24C2-62, presented elsewhere [7].
Admittance spectra of the thinner sample 24C2-62 - HFCVD deposited - show a constant conductance plateau on the low frequency side, whereas the slope of the frequency dependent regime approaches the unity for higher frequencies, at lower temperatures. Moreover, the threshold frequency, where dispersive regime begins, moves at higher frequencies when the temperature increases. Such a behavior is well described by the so called augmented Jonscher expression [12]

\[ G(\nu, T) = G_{dc}(T) \left\{ 1 + \left[ \nu / \nu_c(T) \right]^n \right\} + A \nu. \]  

(2)

Here \( G_{dc} \) and \( \nu_c \) are the DC conductance and the characteristic relaxation frequency corresponding to the onset of conductance dispersion, \( n \) is a fractional exponent and \( A \) is a constant which can show a weak temperature dependence. In this expression, the first term is commonly related to a conduction mechanism involving charge displacement, indicated by the parameters \( G_{dc} \) and \( \nu_c \) which are thermally activated. The second term of Eq.(2), which corresponds to the nearly constant loss widely discussed by many authors [13-14], becomes dominant at sufficiently low temperatures or at higher frequencies. This term is related to charge carriers relaxation inside a potential well when their energies are not sufficient to activate a conduction mechanism over the well, with a real charge displacement. In a previous work on sample 24C2-62 [7], we found \( A=1.6\pm0.3\times10^{12} \) S/Hz and \( n =0.66\pm0.05 \), whereas
$G_{dc}$ and $\nu_c$ showed the superposition of two exponential regimes. A common activation energy equal to 1.25±0.05 eV was found for higher temperatures, whereas two different values equal to 0.55±0.05 eV and 0.62±0.05 eV were found for lower ones. Taking a glance at curves in figure 1, it is possible to recognize full correspondence with regimes described by Jonscher expression: constant conductance plateau, increasing low-frequency regime with slope 0.5, high frequency regime with unitary slope. An additional contribution with slope 0.2 at intermediate frequencies, is strongly apparent in measurements carried out above 525 K. This regime extends over a wider frequency range with a temperature rise. A similar behavior in the conductance spectrum has been already observed in diluted ionic conductors [15]. In polycrystalline diamond, this effect could be related to blocking effects of Schottky barriers at grain surfaces, as advanced in similar polycrystalline systems for interface regions [16]. In the frequency decade 10^6-10^7 Hz, real admittance shows an increasing trend with slope larger than unity. This behavior was tentatively related to a metal-like resistance in series with the sample, due to the holding scheme used for measurements.

**Figure 2.** Angular frequency dependence of imaginary part of impedance and electric modulus of sample 24C2-62 in the 325-625 K range with 50 K steps. Open symbols correspond to $M''$.

Inset of figure 1 shows the imaginary part of admittance. Two different transport mechanisms, leading to different capacitance values were found. In the high frequency limit, a total capacitance of
$C_H = 2.66 \pm 0.02 \text{ pF}$ was calculated whereas, in the low frequency regime, a total capacitance changing from $C_L(616\text{ K}) = 1.98 \pm 0.02 \text{ nF}$ to $C_L(525\text{ K}) = 0.37 \pm 0.05 \text{ pF}$ was evaluated. Transition frequencies with the corresponding conductance values (white open dots on the curves) were taken to evaluate the associated activation energies. A barrier height equal to $1.60 \pm 0.05 \text{ eV}$ was calculated, which fairly agrees with the estimated $G_{dc}$ temperature dependence.

**Figure 3.** Reduced imaginary part of impedance and electric modulus of sample Ka8-105 versus reduced frequency, at several temperatures. Full symbols correspond to $M''$.

Let’s again consider the system composed of two phases: grains and GBs in parallel. The imaginary parts of impedance and electric modulus of such a heterogeneous system can be represented by the superposition of Lorentzian peaks (i.e. Debye’s peaks) whose expression is

$$Z''(\omega, T) = \sum_m R_m \frac{\omega \tau_m}{1 + (\omega \tau_m)^2}$$

(3)

Interfacial Nanostructures in Ceramics: a Multiscale Approach IOP Publishing
Journal of Physics: Conference Series 94 (2008) 012009
doi:10.1088/1742-6596/94/1/012009
\[ M''(\omega, T) = \sum_{m} C_{m} \frac{\omega \tau_{m}}{C_{m} + (\omega \tau_{m})^2}. \]  

Debye’s peaks assume the maximum value at \( \omega \tau_{m} = \omega R_{m} C_{m} = 1 \). In such conditions, amplitude of each \( Z' \) peak corresponds to \( R_{m}/2 \Omega \), whereas amplitude of \( M'' \) peaks correspond to the value \( C_{m}/2C_{m} \). Imaginary impedance and electric modulus spectra are shown in figure 2 for 24C2-62 sample. It is found that frequencies at maximum \( Z' \) peaks do not correspond to the maximum of \( M'' \) curves. A careful analysis of curves at 625 K, give us the possibility to evidence as, around \( 10^4 \) rad/s, a small contribution in \( M'' \) curve is present, which corresponds to \( Z'' \) peak. In order to compare peaks height and frequency for different samples, impedance and frequency data are scaled to the lower frequency value of impedance and to \( \sigma_{dc} T \), respectively. This kind of scaling was suggested by Summerfield [17] and indicates the time temperature superposition principle (TTSP). \( \sigma_{dc} \) is the DC conductivity at the lower frequency for each temperature T. Reduced imaginary impedance and electric modulus spectra are shown in figure 3 for Ka8-105 sample.

It appears clearly that curves satisfy to TTSP, but they result from the composition of more than one peak and, at the moment, it is hard to say how many. However the correspondence of at least one peak in normalized \( Z' \) and \( M'' \) curves clearly appears. If we associate each peak with a sample phase, by comparison with an equivalent electric circuit, we can gain a better understanding of the response to small amplitude AC signals. To this aim, we have made complex nonlinear least squares (CNLS) fits of original curves (real and imaginary part of impedance) by comparison with the response of an electric equivalent circuit, by using commercially available software [18]. Fairly good matches were obtained with a scheme composed by three Voigt’s elements, representing grain, GB and grain surface related effects. Since we expect a distribution of grain size, Voigt’s element associated to the grain phase has been put in parallel with a constant phase element (CPE). Peak frequencies, \( 1/\tau_{m} \), corresponding to resolved components, have been pointed out in Table 1 for both analyzed samples at a temperature of 525K together with the corresponding reduced angular frequency, \( \omega_{mN} \), where \( \omega_{mN} = 2\pi (1/\tau_{m})/(\sigma_{dc} T) \).

| Table I | 24C2-62 | Ka8-105 |
|---------|---------|---------|
| peak    | \( 1/\tau_{m} \) (s\(^{-1}\)) | \( \omega_{mN} \) (rad*cm/S/K/s) | \( 1/\tau_{m} \) (s\(^{-1}\)) | \( \omega_{mN} \) (rad*cm/S/K/s) |
| 1°      | 46      | 6 \times 10^4 | 6 \times 10^4 | 1.8 \times 10^7 |
| 2°      | 961 CPE | 1.3 \times 10^{10} CPE | 6 CPE | 1.8 \times 10^{10} CPE |
| 3°      | 1 \times 10^9 | 1.3 \times 10^{11} | --- | --- |

Table 1. Peak frequency, \( 1/\tau_{m} \), and reduced angular frequency, \( \omega_{mN} \), corresponding to fit resolved components for both 24C2-62 and Ka8-105 response at 525K.

It is worth to note the correspondence of reduced frequencies of the second peak for both samples, namely: \( (1.5\pm0.3) \times 10^{10} \) rad/s*cm/S*K\(^{-1}\). The first peak in sample Ka8-105 seems to be better resolved in frequency, not so much influencing the position of the second peak, with respect to sample 24C2-62, where they are less than one decade apart. Since samples under study, although different in morphology and structure, have certainly a common grain phase, constituted by well formed diamond domains with a fairly similar average size perpendicularly to the growth direction, we believe to have singled out the peak associated to this phase in each sample. Such peaks can be distinguished from other contributions because, for each analyzed specimen, the corresponding Voigt element contains a constant phase element in parallel. The first peak can therefore be related to the GBs phase whereas the third contribution might be associated to grain surface related effects, like depletion layers and...
surface Schottky barriers. Imaginary part of impedance data and fit results are plotted in figure 4 for Ka8-105 at different temperatures.

![Graph showing frequency dependence of imaginary part of impedance of Ka8-105 sample (symbols). Continuous lines correspond to CNLS fit. Inset. The same for 24C2-62 sample, at several temperatures.](image)

**Figure 4.** Frequency dependence of imaginary part of impedance of Ka8-105 sample (symbols). Continuous lines correspond to CNLS fit. Inset. The same for 24C2-62 sample, at several temperatures.

A good agreement is obtained; with a better fits quality in the middle frequencies than in the lower and higher frequencies regimes, where electrodes polarization might affect measurements. Temperature dependence of peak frequencies, derived from Ka8-105 data fit, is presented in figure 5. Two activation energy values were found. The first value, equal to 1.6±0.1 eV, is reasonably related to the diamond grain Fermi level, usually located above the valence band for unintentionally doped samples. The second one, equal to 1.0±0.1 eV, is associated to an average barrier height related to GBs. If we consider the high temperature limit of the second peak of table 1, here associated to the grain phase and to the activation energy of 1.6±0.1 eV, the free oscillation phonon frequency can be estimated to 1.0×10^{12} Hz, in good agreement with literature data. Figure 6 displays the Arrhenius plot of second peak frequencies resulting from fits on sample 24C2-62. Also in this case two activation energy values were found: 0.6±0.1 eV and 1.3±0.1 eV. Frequencies corresponding to the first and third peak are not plotted for clarity, they show a common energy barrier equal to 0.6±0.1 eV. The smaller value is believed to be associated to GBs barrier height whereas the larger one is associated to the grain phase. It is noteworthy that, also in this case, a phonon frequency equal to 1.9×10^{13} Hz can be extrapolated from data of Figure 6 in the high temperature limit where the grain contribute is dominant. This analysis points out the better quality of Ka8-105 film, deposited by MWCVD,
compared with 24C2-62 sample, deposited by HF assisted CVD. The better quality is undoubtedly related to the larger average grain sizes of such film and to the optimized deposition conditions.

\[
\frac{1}{\tau_m} \propto \frac{1}{T}
\]

\[
E_a = 1.0 \pm 0.1 \text{ eV}
\]

\[
E_a = 1.6 \pm 0.1 \text{ eV}
\]

\[
F\text{igure 5. Arrhenius plot of evaluated time constant (}\tau_m = R_mC_m\text{) resulting from fitting Ka8-105 data, reported in figure 4, with the superposition of three Debye’s peaks as in expression (3).}
\]

Let us consider now peaks associated to the GBs phase. Corresponding frequencies, considered at different temperatures, display smaller activation energy if compared with the previous ones: 1.0±0.1eV and 0.6±0.1eV for Ka8-105 and 24C2-62, respectively. The great difference between activation energies of the two samples, indicates a different structure and composition of this phase. In agreement with other authors, this evidences the influence of the deposition technique on sample morphology: in presence of oxygen Ka8-105 sample shows a lower presence of sp\(^2\) bonds. Moreover, the third peak really seems to us of different kind, as also displayed by the estimated activation energies. Indeed activation energy for the thicker film is similar to that of the grain whereas, in the other sample, it corresponds to the GBs activation energy. Such a contribution might arise from surface related effects as blocking barriers at grain interfaces. In any case Ka8-105 data, presented in a logarithmic Cole-Cole plot give evidence of a high frequency contribution from a metal-like series resistance, probably associated to the holding scheme. This contribution was considered in Ka8-105.
fits adding a series resistance to the previous discussed model. It results a resistance varying from 83 Ω to 210 Ω in the range 525-616 K, showing clearly a metallic behavior.

![Arrhenius plot](image)

**Figure 6.** Arrhenius plot of evaluated time constant ($\tau_m = R_mC_m$) of the second contribution resulting from fitting procedure on 24C2-62.

Finally, we would like to introduce and discuss dielectric relaxations of the different samples. Real part of permittivity is plotted in figure 7 for both samples. Looking at the plot of real permittivity it is apparent, at the lower frequencies, the $1/\omega$ behavior usually associated to the electrode polarization but also the great difference in magnitude (more than an order) of the permittivity change, $\Delta \varepsilon = \varepsilon_\infty - \varepsilon$, due to relaxations [19]. Thicker sample shows the least permittivity dispersion and very nearly approaches natural diamond permittivity (i.e. 5.5) whereas thinner sample, around room temperature, had not completely relaxed yet.

4. **Conclusioni**

A detailed analysis of admittance data was pursued. Three different regimes common to both samples were found using the augmented Jonscher expression as reference. A fourth behavior characteristic of the thicker CVD diamond film, expected of better quality and with bigger diamond grains, was evidenced and related to blocking effects of Schottky barriers at grain surfaces. An independent determination of activation energies, relative to $G_{dc}$ and to imaginary admittance frequencies
corresponding to the transition between the high and low frequency limit, provided the same value for barrier height associated to the grain phase. Furthermore, using $Z''$ and $M''$ representation and fits with three Voigt elements it has been possible to identify univocally grain and grain boundary phases. A third phase, with more elusive characteristics, was also identified. Finally, dispersion analysis highlighted a large value of permittivity directly related to grain boundary contribution.

![Figure 7](image)

**Figure 7.** Real part of permittivity, $\varepsilon'$, for both samples (24C2-62 square, Ka8-105 circle) at 525K (full symbols) and 325 (open symbols) for 24C2-62 sample only.

**Acknowledgement**
Authors sincerely acknowledge P. Ascarelli and R. Kalish for providing samples used in this work.

**References**
[1] Kubovic M, Kasu M, Kallfass I, Neuburger M, Aleksov A, Koley G, Spencer M G and Kohn E 2004 *Diamond Relat. Mater.* 13 802
[2] Spaziani F, Rossi M C, Conte G, Lavanga S, Lanzieri C, Cetronio A and Ralchenko V 2007
Diamond Relat. Mater 16 1016

[3] Ralchenko V [personal communication]

[4] Conte G, Rossi M C, Salvatori S, Tersigni F, Ascarelli P and Cappelli E 2003 Appl. Phys. Lett., 82 4459

[5] Fiegl B, Kuhnert R, Ben-Chorin M, Koch F 1994 Appl. Phys. Lett. 65 371

[6] Bataineh M M and Reinhard D K 1997 Diamond Relat. Mater. 6 1689

[7] Feliciangeli M C, Rossi M C and Conte G 2007 Diamond Relat. Mater. 16 930

[8] Heidger S, Fries-Carr S, Weimer J, Jordan B and Wu R 1998 IEEE 98 0-7803-4449-9

[9] Conte G, Rossi MC, Salvatori S, Fabbri F, Loreti S, Ascarelli P, Cappelli E, Trucchi D 2003 J. Appl. Phys., 93 6078

[10] Ascarelli P, Cappelli E, Mattei G, Pinzari F and Martelli S 1995 Diamond Relat. Mater. 4 464

[11] Avigal Y, Richter V, Fizgeer B, Saguy C, Kalish R 2004 Diamond Rel. Mater. 13 1674

[12] Schroder T B and Dyre J C 2000 Phys. Rev. Lett. 84 310

[13] Leon C, Rivera A, Varez A, Sanz J, Santamaria J and Ngai K L 2001 Phys. Rev. Lett. 86 1279

[14] Sidebottom D L 2005 Phys. Rev. B 71 134206

[15] Nowick A S and Lim B S 2001 Phys. Rev. B 63 184115

[16] Ahmad M M, Yamada K and Okuda T 2002 Solid State Communications 123 185

[17] Summerfield S. 1985 Philos. Mag. B 52 9

[18] ZsImWin 3.10 by EChem Software

[19] Sidebottom D L 2000 Phys. Rev. B 61 14507