ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

Thin Solid Films 516 (2007) 340–344

www.elsevier.com/locate/tsf

Characteristics of low-*k* SiOC(–H) films deposited at various substrate temperature by PECVD using DMDMS/O_2 precursor

Chang Young Kim [a], Seung Hyun Kim [a], R. Navamathavan [a], Chi Kyu Choi [a,*], Won Young Jeung [b]

[a] *Nano Thin Film Materials Laboratory, Department of Physics, Cheju National University, Ara 1 Dong, Jeju, 690-756, South Korea*
[b] *Advanced Materials Division, Korean Institute of Science and Technology, Seoul, 130-650, South Korea*

Available online 18 June 2007

Abstract

We report on the influence of substrate temperature on SiOC(–H) thin films deposited on *p*-type Si(100) substrates by plasma enhanced chemical vapor deposition (PECVD) with dimethoxydimethylsilane (DMDMS) and oxygen gas as precursors. The films were deposited at various substrate temperatures with a radio frequency (rf) power of 500 W and working pressure of 700 mTorr. Fourier transform infrared (FTIR) spectroscopy was used in the absorbance mode over the range of 400 to 4000 cm^{-1} which showed the various bonding configurations such as Si–O–Si(C), Si–CH_3, –OH, and CH_x bonds in the SiOC(–H) films. The X-ray photoelectron spectroscopy (XPS) was used to study the binding energies of Si–C, SiO–C_3, SiO_2–C_2, SiO_3–C, Si–O_2, C–C, C–H and C–O bonds in the SiOC(–H) films as a function of the substrate temperature. The dielectric constant of the SiOC(–H) films was measured using a metal insulator semiconductor (MIS, Al/SiOC(–H)/*p*-Si) structure at 1 MHz frequency. The lowest dielectric constant of the films deposited at room temperature was 2.22 and was achieved with DMDMS/O_2 precursor.
© 2007 Elsevier B.V. All rights reserved.

PACS: 77.55.+f; 77.22.–d; 81.15.Gh; 78.55.Mb
Keywords: Low-*k* material; SiOC(–H) films; DMDMS; PECVD; FTIR; XPS

1. Introduction

In the last few years, there has been increasing research activity focused on low dielectric constant (low-*k*) materials due to their potential use in the microelectronics industry [1–3]. With decreasing feature size, the signal delay and noise also increase due to capacitive coupling and cross-talk noise between the metal interconnections. One way to tackle these problems is to introduce higher performance interlayer dielectric (ILD) coatings. Thus, low-*k* dielectric materials are becoming important in integrated circuits (IC) technology, especially for fabricating dynamic random access memories (DRAM).

Some of the potential candidate materials to be used as an ILD are organic and inorganic precursors such as hydrogensilsequioxane (HSQ), silsesquioxane (SSQ), methylsilsisequioxane (MSQ) and carbon doped silicon oxide (SiOCH) [4–8]. Among these, SiOC(–H) films are widely preferred by the semiconductor industry because of their excellent properties. It has been shown that organic functional groups can dramatically decrease dielectric constant by increasing the free volume of films [9]. The incorporation of doping elements such as carbon and hydrogen can be found to play a crucial role in lowering the value of the dielectric constant of the film. In fact, the ability of these elements in modifying the local structure of the silicon oxide network gives rise to a lower density material. In other words, the replacement of Si–O bonds with Si–CH_3 (methyl group) bonds causes bulk porosity due to the formation of nano-sized voids within the silicon oxide matrix [10,11]. The SiOC(–H) films can be fabricated by using plasma polymerization in an inexpensive way that results in a homogeneous, highly cross-linked and thermally stable films for interconnect applications. In this present study, we investigated the deposition and structural characterization of low-*k* SiOC(–H) thin films deposited with different substrate temperature by using DMDMS and oxygen as precursors.

2. Experimental

SiOC(–H) thin films were deposited on *p*-Si(100) substrates by using a mixture of DMDMS ($C_4H_{12}O_2Si$) and oxygen gases as precursors in a plasma enhanced chemical vapor deposition (PECVD) system at different substrate temperatures. Before

* Corresponding author.
E-mail address: cckyu@cheju.ac.kr (C.K. Choi).

0040-6090/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2007.06.097

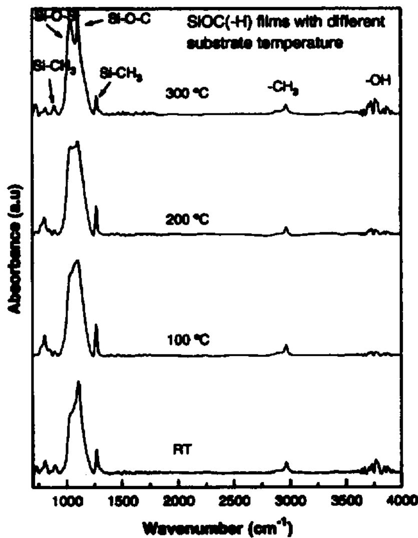

Fig. 1. FTIR spectra of as-deposited SiOC(–H) films with different substrate temperature.

depositing the thin films, we evacuated the chamber to a pressure less than 10^{-6} Torr, and we maintained the working pressure at 700 mTorr. The plasma was generated using radio frequency (rf) power supply with a frequency of 13.56 MHz

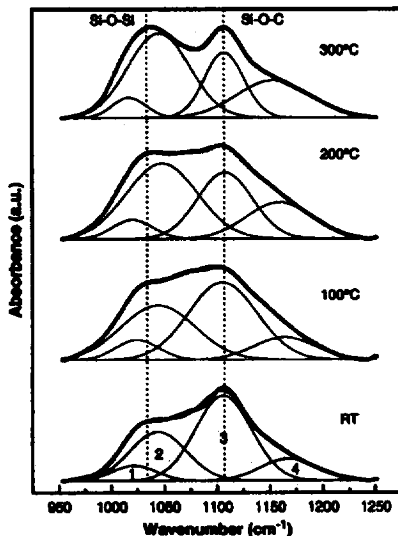

Fig. 2. Deconvolution of FTIR spectra of as-deposited SiOC(–H) films with different substrate temperature between the wavenumber region of 950–1250 cm^{-1}.

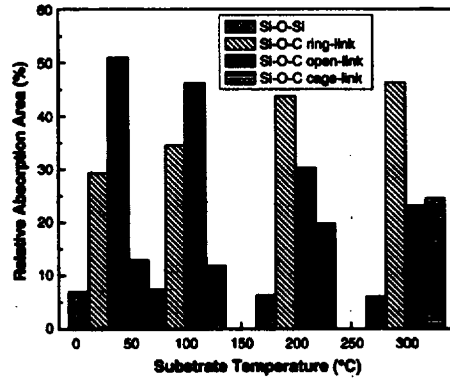

Fig. 3. Relative absorption area of Si–O–Si stretching, Si–O–C ring-link, Si–O–C open-link and Si–O–C cage-link structure as a function of substrate temperature.

between the two electrodes. The rf power supply was maintained at 500 W. The DMDMS precursor was introduced into the chamber via Ar gas, which was controlled by using a mass-flow controller. The total flow rate of the precursors was maintained as 50 sccm and the flow rate ratio of [DMDMS/(O_2+DMDMS)] × 100% was fixed at 80%. In order to prevent the recondensation of DMDMS precursor, we heated the bubbler bath and all of the gas delivery lines, and kept them at a constant temperature of 60 °C. The DMDMS precursor is a clear liquid with a boiling point of 82 °C and a density of 0.865 gm/cm^3.

The refractive index and the thickness of the deposited films were measured by using an ellipsometer (Gaertner L116D) at a wavelength of 632.8 nm and a field emission scanning electron microscope (FESEM, JSM-6700F), respectively. To investigate the chemical bonding structure, atomic concentration and binding energy of SiOC(–H) films, FTIR spectroscopy (Bruker, IFS-120HR/FRA-106S) in absorbance mode and XPS (ESCA Lab-2000) were used. All the FTIR absorption spectra were acquired with a resolution of 2 cm^{-1} by using a Si wafer as a reference. The number of scans was automatically chosen and

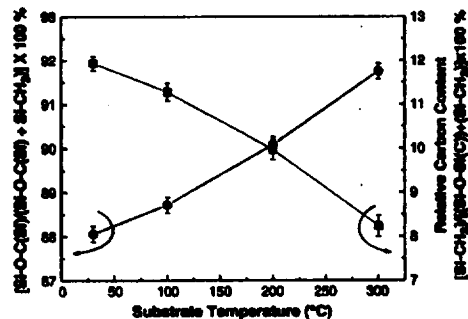

Fig. 4. Relative carbon and Si–O–C(Si) concentration (%) of the SiOC(–H) films deposited with different substrate temperature.

averaged for each spectrum in order to ensure an optimal signal-to-noise ratio. To compare the spectra, we subtracted a proper baseline from all the recorded FTIR spectra. The XPS analyses were conducted with ESCA-2000, VG Microtech Ltd., West Sussex, UK system with computer equipped with vision software. The X-ray source was a monochromatic Al kα (1486.6 eV) anode kept at 14 kV and 20 mA. An analyzer pass energy of 50 eV was used. The base pressure in the analysis chamber was 5×10^{-9} Torr. The dielectric constant at 1 MHz was investigated with a metal insulator semiconductor (MIS, Al/SiOC(–H)/p-Si(100)) structure.

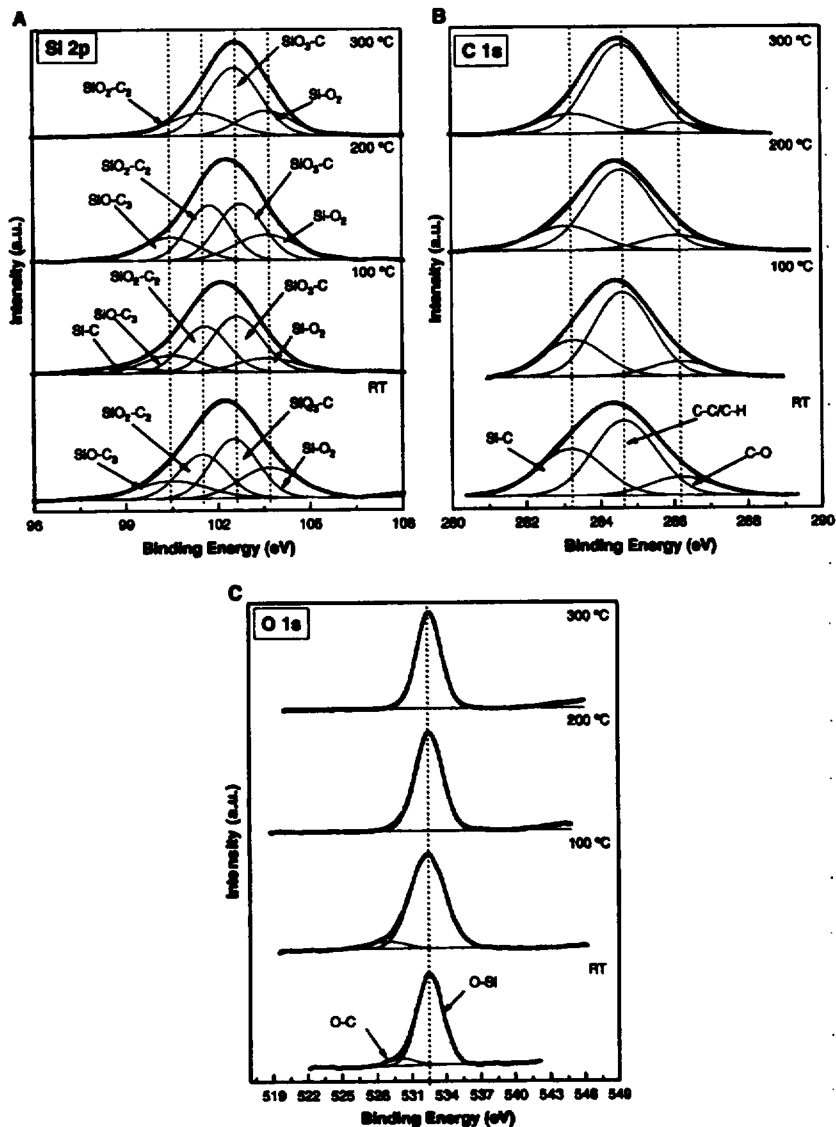

Fig. 5. XPS narrow scans spectra of the SiOC(–H) films deposited with different substrate temperature: (A) Si 2p electron orbital, (B) C 1s electron orbital and (C) O 1s electron orbital.

3. Results and discussion

Fig. 1 shows the FTIR spectra of SiOC(–H) films deposited at various substrate temperatures. The characteristic band of the SiOC(–H) film showed absorption bands due to Si–O–Si (around 1040 cm^{-1}), Si–O–C (around 1106 cm^{-1}), Si–CH_3 (around 800 and 950 cm^{-1}; 1250 and 1300 cm^{-1}) and –OH (3700–3800 cm^{-1}) in addition to those of the Si substrate. There is shoulder at about 1160 cm^{-1} in all the absorption spectra, which is assigned to a broad Si–O–C peak, and corresponds to the Si–O–C cage-link structure, resulting in more porous nature in the SiOC(–H) film [10–12]. As the substrate temperature increased, the intensity of Si–CH_3 bond decreased, demonstrating that more oxygen atoms are incorporated into the Si–O–C ring-link network. The precursors are dissociated into highly reactive species that form the SiOC(–H) films with the clearly separated absorbance peaks of the Si–O–Si and the Si–O–C bands. With increasing substrate temperature, the Si–O–Si peak becomes stronger due to rearrangement of bonding configuration. It is one of the characteristic peaks of the infrared spectrum for the SiOC(–H) film.

The broad band spectra from 950 to 1250 cm^{-1} consists of overlapping vibration modes from various bond structures. In order to understand the bonding configuration of SiOC(–H) films, we deconvoluted the FTIR spectra into its four constituents, as shown in Fig. 2. The bands with peaks centered at 1021, 1045, 1106 and 1160 cm^{-1} are assigned to Si–O–Si stretching vibration, Si–O–C ring-link, open-link and cage-link structure, respectively. From this deconvoluted data, the relative absorption area of each bonding structure was deduced. Fig. 3 shows the relative absorption areas of the bonding structures in the SiOC(–H) films as a function of substrate temperature. This result shows that the Si–O–Si stretching mode almost remains constant (about 7%) whereas the Si–O–C ring-link structure increased (from 29.22 to 46.34%) with the increase of substrate temperature. The Si–O–C open-link structure decreased (from 50.94 to 23.11%) while that of cage-link structure was increased (from 12.88 to 24.48%) with the increase of substrate temperature. As the substrate temperature increased, the number of cage-link structure in the SiOC(–H) film increased due to the incorporation of carbon atoms into the Si–O–Si network.

Fig. 4 shows the relative carbon and Si–O–C(Si) content present in the SiOC(–H) film as a function of the substrate temperature. The relative carbon content is calculated by the following equation normalized to the peak height of the Si–O–Si stretch mode in the FTIR spectra [13].Relative carbon content (%)=$[A_c/(A_o+A_c)]\times 100\%$, where A_c and A_o are the absorption peak areas of Si–CH_3 stretching mode (from 800 to 950 cm^{-1} and from 1250 to 1300 cm^{-1}) and the absorption peak area of Si–O–Si (from 900 to 1250 cm^{-1}), respectively. The relative content of carbon atoms decreased from 11.85 to 8.5% as the substrate temperature increased from room temperature to 300 °C. However, the Si–O–Si stretching mode increases with increase of substrate temperature.

In order to understand the bonding configurations of SiOC(–H) films in detail, XPS analysis was further employed. Fig. 5(A)–(C) shows the XPS narrow scans of C 1s, Si 2p and O 1s electron orbital of the SiOC(–H) films prepared with different substrate temperature. The XPS narrow scan spectra were deconvoluted by fitting the data with a number of Gaussian peaks. The Si 2p electron orbital spectra consisted of five peaks as shown in Fig. 5(A) that were assigned to Si–C (98.7 eV), SiO–C_3 (100.5±0.1 eV), SiO_2–C_2 (101.6±0.1 eV), SiO_3–C (102.6±0.1 eV) and Si–O_2 (103.6 eV) [14,15] for the SiOC(–H) deposited at room temperature. The binding energies that have been reported in previous studies are a little different from each other and the fitting procedure is somewhat arbitrary, but it is worth distinguishing the silicon in different states [16–18]. As the substrate temperature increased, the intensities of SiO_2–C_2 and SiO_3–C bonds were increased due to the bonding rearrangement at elevated temperatures. This result is in good agreement with that of FTIR data in which the intensity of Si–O–C ring-link structure was found to be increased. The SiOC(–H) films become oxygen rich as we increase the substrate temperature, this is due to Si–C bonds broken at the elevated substrate temperatures leaving Si–O bonds dominant in the film. This is because the binding energy of the Si–C bond is lower than that of the Si–O bond [19]. The high relative percentage of O–Si–C peak in the Si 2p spectra indicates that randomly amorphous C–Si–O network dominated in the SiOC(–H) film. The various binding energies used for identification of the chemical groups are shown in Table 1.

Fig. 5(B) shows the C 1s electron orbital XPS narrow scan spectra of SiOC(–H) films deposited at different substrate temperature which comprises of three bond components namely, Si–C (283.3±0.1 eV), C–C/C–H (284.6 eV), and C–O (286.2±0.1 eV) [20,21] for the films deposited at different substrate temperature. It is interestingly observed that slight chemical shift in the binding energies in the bonding structure as the substrate temperature increased which corresponds to the oxygen rich SiOC(–H) films. Fig. 5(C) shows the O 1s electron orbital XPS narrow scan spectra of SiOC(–H) films deposited at different substrate temperature which is decomposed into two components namely, O–C (530.1±0.1 eV) and O–Si (532.6 eV) [22],

Table 1
The Si 2p, C 1s, and O 1s electron binding energies of the SiOC(–H) films

Substrate temperature	Si 2p (eV)					Ref.	C 1s (eV)			Ref.	O 1s (eV)		Ref.
	Si–C	SiO–C_3	SiO_2–C_2	SiO_3–C	Si–O_2		Si–C	C–C/C–H	C–O		O–C	O–Si	
RT	–	100.4	101.4	102.5	103.6	14,15	283.2	284.6	286.2	20,21	530.1	532.6	22
100 °C	98.7	100.4	101.5	102.6	103.6		283.2	284.6	286.2		530	532.6	
200 °C	–	100.4	101.7	102.7	103.6		283.1	284.6	286.1		–	532.6	
300 °C	–	–	101.6	102.7	103.6		283.2	284.6	286.1		–	532.6	

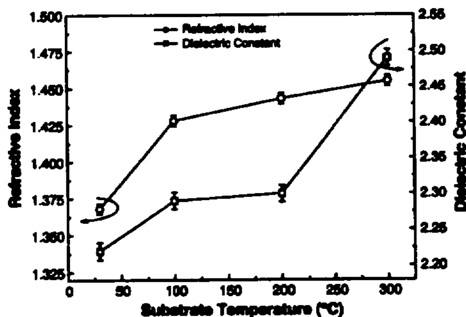

Fig. 6. Refractive index and dielectric constant of the SiOC(–H) films as a function of substrate temperature.

except for the film deposited at 200 and 300 °C. For the film deposited at 200 and 300 °C, the O 1s narrow scan spectrum is well fitted into one peak at 532.6 eV (O–Si). This result means that more oxygen atoms are attached to the Si–O chain thus forming SiOC(–H) film at higher substrate temperature. The XPS narrow scans of Si 2p, C 1s and O 1s spectra suggest that the major part of Si in the SiOC(–H) film is bonded with oxygen atoms to form an expected randomly Si–O–Si network. The XPS data is in good agreement with that of FTIR data showing the presence of cage-linked structure in the SiOC(–H) film.

Fig. 6 shows the refractive index and dielectric constant of the SiOC(–H) films as a function of various substrate temperature. It is found a trend that both the refractive index and dielectric constant increase slightly with substrate temperature. The value of refractive index and dielectric constant of the SiOC(–H) films deposited at different substrate temperatures is found to increase from 1.368 to 1.455 and 2.22 to 2.49, respectively, as the substrate temperature increases from room temperature to 300 °C. Comparing the structural behavior as observed from FTIR and XPS data, it is evident that enhancement of oxygen rich atoms at higher substrate temperature in the SiOC(–H) film result in a slight increase of dielectric constant. This is attributed to the lower carbon concentration due to Si–CH_3 bonds broken at elevated substrate temperature that give rise to the increase of dielectric constant. This can be explained by two factors: the decrease of voids and the increase of ionic polarization by decreasing Si–CH_3 bonds [13,23]. Therefore, at higher substrate temperature, the weaker Si–CH_3 and C–H bonds broken leaving the films with a lower concentration of these bonds, and the SiOC(–H) films become more oxygen rich.

4. Conclusions

SiOC(–H) thin films with low dielectric constant were deposited at various substrate temperature on a *p*-Si(100) substrates by using PECVD with a mixture of DMDMS and oxygen gases. The influence of substrate temperature on the properties of the SiOC(–H) films was investigated. The chemical and structural nature of these films was characterized by using XPS and FTIR. The results indicated that the SiOC(–H) films exhibit clearly distinguished bonds of Si–O–Si and Si–O–C. As the substrate temperature increased the dielectric constant of SiOC(–H) film increased due to Si–C bonds broken leaving Si–O bonds rich in the film. The lowest dielectric constant of the SiOC(–H) films deposited at room temperature achieved with DMDMS/O_2 precursor was found to be 2.22.

Acknowledgements

This research was performed for the Nuclear R; D programs funded by the Ministry of Science and Technology (MOST) of Korea. This work was also supported by "System IC 2010" project of Korea Ministry of Commerce, Industry and Energy. The researchers involved in this study were supported by the grant from "the 2nd Stage BK-21 Project". And this work was also supported by the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korea Government (MOST), (No. R01-2007-000-10181-0).

References

[1] Y. Xu, Y. Tsai, K.N. Tu, B. Zhao, Q.Z. Liu, M. Brongo, G.T.T. Sheng, C.H. Tung, Appl. Phys. Lett. 75 (1999) 853.
[2] K. Maex, M.R. Baklanov, D. Shamiryan, F. Lacopi, S.H. Brongersma, Z.S. Yanovitskaya, J. Appl. Phys. 93 (2003) 8790.
[3] K. Endo, K. Shinoda, T. Tatsumi, J. Appl. Phys. 86 (1999) 2739.
[4] C.S. Yang, K.S. Oh, J.Y. Ryu, D.C. Kim, S.Y. Jing, C.K. Choi, Thin Solid Films 390 (2001) 113.
[5] A. Grill, V. Patel, Mater. Res. Soc. Symp. Proc. 612 (2000) D2.9.1.
[6] C.S. Yang, Y.H. Yu, K.M. Lee, H.J. Lee, C.K. Choi, Thin Solid Films 435 (2003) 165.
[7] C.H. Ting, T.E. Seidel, Mater. Res. Soc. Symp. 381 (1995) 3.
[8] A. Grill, V. Patel, Appl. Phys. Lett. 85 (1999) 6.
[9] L.M. Han, J.S. Pan, S.M. Chen, N. Balasubramanian, J. Shi, L.S. Wong, P.D. Foo, J. Electrochem. Soc. 148 (2001) F148.
[10] A. Grill, D.A. Neumayer, J. Appl. Phys. 94 (2003) 6697.
[11] A. Grill, V. Patel, Appl. Phys. Lett. 79 (2001) 803.
[12] Y.L. Cheng, Y.L. Wang, G.J. Hwang, M.L. O'Neill, E.J. Karwacki, P.T. Liu, C.F. Chen, Surf. Coat. Technol. 200 (2006) 3134.
[13] Y.H. Kim, S.K. lee, H.J. Kim, J. Vac. Sci. Technol., A 18 (2000) 1216.
[14] C. Onneby, C.G. Pantano, J. Vac. Sci. Technol., A 15 (1997) 1597.
[15] J. Heo, H.J. Kim, J.H. Han, J.W. Shon, Thin Solid Films 515 (2007) 5035.
[16] Y.H. Wang, M.R. Moitreyee, R. Kumar, L. Shen, K.Y. Zeng, J.W. Chai, J.S. Pan, Thin Solid Films 460 (2004) 211.
[17] Y.H. Wang, J. Lin, C.H.A. Chua, Mater. Sci. Eng., B 95 (2002) 43.
[18] L.M. Han, J. Pan, S. Chen, N. Balasubramanian, J. Shi, L.S. Wong, P.D. Foo, J. Electrochem. Soc. 148 (2001) F148.
[19] C. Radtke, I.J.R. Baumvol, J. Morais, F.C. Stedile, Appl. Phys. Lett. 78 (2001) 3601.
[20] H. Li, T. Xu, C. Wang, J. Chen, H. Zhou, H. Liu, Diamond Relat. Mater. 15 (2006) 1585.
[21] J.F. Zhao, P. Lemoine, Z.H. Liu, J.P. Quinn, P. Maguire, J.A. McLaughlin, Diamond Relat. Mater. 10 (2001) 1070.
[22] S.Y. Jing, H.J. Lee, C.K. Choi, J. Korean Phys. Soc. 41 (2002) 769.
[23] T.K.S. Wong, B. Liu, B. Narayanan, V. Ligatchev, R. Kumar, Thin Solid Films 462–463 (2004) 156.