

# Structural characterization of TiAl-doped DLC Coatings by Raman spectroscopy and X-ray photoelectron spectroscopy

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## Abstract

In this work, the combinations of TiAl-doped diamond-like carbon (DLC) and TiAlN/TiN double-layered films were designed to deposit on the tool steels using cathodic arc evaporation in a single process. The economic advantage in depositing the combined coating in one production scale PVD coating system is of practical importance. The TiAl-doped DLC as lubricant coatings were synthesized with TiAl-target arc sources to emit ion plasma to activate acetylene ( $C_2H_2$ ) reactive gases. Scanning electron microscopy (SEM), micro-Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) techniques were employed to analysis the microstructure properties of TiAl-doped DLC coatings. Vicker's hardness tester was used to measure the mechanical properties of TiAl-doped DLC coatings. The results show that the microhardness of TiAl-doped DLC coatings was dependent on the ratio of  $I_D/I_G$  and  $sp^3/sp^2$ , which higher  $sp^3/sp^2$  ratio or lower  $I_D/I_G$  ratio with higher hardness value.

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## Introduction

A new trend of PVD protective coatings for tribological applications was recently developed with duplex or combination coatings and multi-layered coatings [1-8]. An interesting approach is to deposit coatings with low friction coefficients as lubricant on top of TiAlN coatings [9-11]. One of the most effective commercial coatings of this type is the multilayered TiAlN/WC-C hard lubricant coating developed by Derflinger et al. [11]. The main advantage of this coating is a very low initial wear rate during the running-in stage of wear that leads to a significant increase in the tool life. In the previous work, it is reported that TiAl-doped DLC coatings synthesized by cathodic arc evaporation (CAE) exhibit extremely low friction coefficient superior to that of TiN, TiCN and TiAlN coatings [12]. A detailed mechanical evaluation of TiAl-doped DLC coatings was carried out in terms of using intensive metal plasma to ignite catalyst reaction of the decomposition of hydrocarbon gases under different flow rate. Similar result reported by Chang et al. [13] that the catalyst effect of three common transition metal plasmas, including Cr, Ti, and Zr, induced the formation of hydrogenated metal-doped DLC films with a mixture of  $sp^3$  and  $sp^2$  carbon bonds. However, the effect of bias voltage and reactive gas partial pressures on

the structural properties of TiAl-doped DLC coatings has not yet found in the literature. It is well known that control of film morphology and mechanical properties is achieved through variation of the substrate bias potential and reactive gas partial pressures, which, in turn modifies the energy and ionization of depositing ions. Typically, for cathodic arc deposition process, substrates are biased negatively in the range of 0 to 300 volts referenced to anode potential [14].

In this work, further studies of the TiAl-doped DLC/TiAlN/TiN multi-layered films on structural characterization were profiled by Raman spectra, X-ray photoelectron spectra (XPS) and Vicker's tester.

## Experimental

Circular specimens were made of tool steels, JIS SKH51 (wt.%) (0.38C, 0.8Si, 13.6Cr, 0.5Mn, 0.3V, Fe balance), which were machined to a diameter of 30 mm and thickness of 5 mm. After heat treatment, the substrate was quenched and tempered in the hardness of HRC 60. The substrates were mechanically ground and polished to have an average roughness  $R_a$  of approximately 0.1  $\mu\text{m}$ . After ultrasonically cleaned in acetone and methane solutions, the samples were then fixed in the chamber holder and subjected to etch and preheat in Ar glow discharge plasma to further remove any contamination on the substrate surfaces.

The pressure of the Ar gas was kept at 0.1 Pa. A dual target cathodic arc evaporation (CAE) system was used to deposit multi-layered films in a single process, as shown in Fig. 1. Titanium and  $Ti_{50}Al_{50}$  target materials were mounted respectively on each side of cathode. Substrate connected to a DC power supply was designed to have bias output varied from  $-50$  V to  $-200$  V during the DLC deposition stages. Another, the chamber pressure with nitrogen reactive gases during interlayer deposition stage of TiN and TiAlN was kept at 3.3 Pa. DLC films were synthesized using only TiAl

target with various flow of acetylene ( $C_2H_2$ ) which led to different partial pressure acted as process parameters in this study. Gradual increase of  $C_2H_2$  partial pressure resulted in TiAl target saturated with carbon so called target poison. The degree of target poisoning was directly related to the TiAl content in DLC layers. The overall coatings were thus designed as TiN interlayer first for 15 minutes, then TiAlN layer as a second layer for 15 minutes, TiAl-doped DLC finally deposited on top for 10 minutes. Details of the deposition process parameters are listed in Table I.

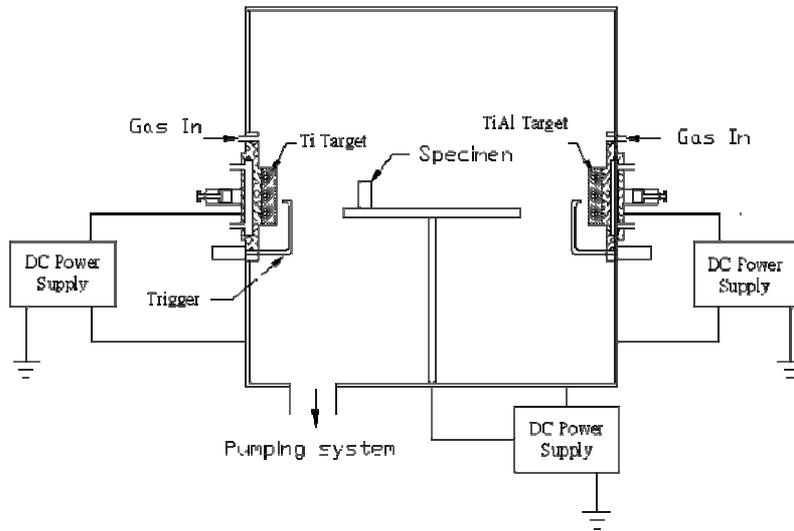


Fig. 1 Schematic of cathodic arc evaporation apparatus

Table I. Process parameters of TiAl-doped DLC/TiAlN/TiN multi-layered films using cathodic arc evaporation

Ar ion bombardment	-1000 V bias for 1 min
H <sub>2</sub> ion bombardment	-1000 V bias for 19 min
Source to substrate distance (cm)	15
Substrate bias voltage (-V)	50, 80, 120, 150, 200, at a fixed C <sub>2</sub> H <sub>2</sub> partial pressure of 2.0 Pa
C <sub>2</sub> H <sub>2</sub> partial pressure (Pa)	1.3, 2.0, 2.6, 3.3, at a fixed bias voltage of -150 V
Substrate temperature (°C)	180~200
Evaporator current (A)	60
Reaction gas	N <sub>2</sub> , C <sub>2</sub> H <sub>2</sub>
Deposition time (min.)	
TiN interlayer	15
TiAlN layer	15
TiAl-doped DLC	10

Cross-section morphology observations of as-deposited specimens were conducted using scanning electron microscopy (SEM; JOEL JSM-5400). Microhardness of the coatings was measured using Vicker's tester under the load of 25 g. Raman spectroscopy using a 50 mW beam of wavelength 514.5 nm from an argon laser in the wavenumber range 1000-2000 cm<sup>-1</sup> was used to identify the I<sub>D</sub>/I<sub>G</sub> bond conversion. X-ray photoelectron spectra were used to identify the sp<sup>3</sup>/sp<sup>2</sup> of chemical bond at the near surface by fitting of C 1s core peak.

## Results and Discussion

### 3.1 Raman spectra

DLC films were synthesized using only

TiAl target with gradual increased flow of acetylene (C<sub>2</sub>H<sub>2</sub>), in addition, various bias voltages and C<sub>2</sub>H<sub>2</sub> partial pressures were chosen as process parameters to study the effects of properties on DLC in this study. In fact, TiAl-doped DLC films were obtained as a result of metal plasma emitted from TiAl target which induced decomposition of C<sub>2</sub>H<sub>2</sub> gas into amorphous carbon layers. During the deposition stage, gradual increase of C<sub>2</sub>H<sub>2</sub> flow poisoning TiAl target with carbon resulted in decrease of TiAl content in DLC layers. Therefore, it is expected that the composition variation of TiAl-doped DLC layers are directly related to the flow of C<sub>2</sub>H<sub>2</sub> gas. A typical SEM observation of cross-sectioned overall film revealed TiAl-doped DLC/TiAlN/TiN

multi-layered structure, as shown in Fig. 2. It clearly appears a dense and compact microstructure of DLC layer compared to that of TiAlN and TiN sub-layers. Large amounts of microparticles can also be seen on the film surface as a result of TiAl droplets ejected from the cathode surface.

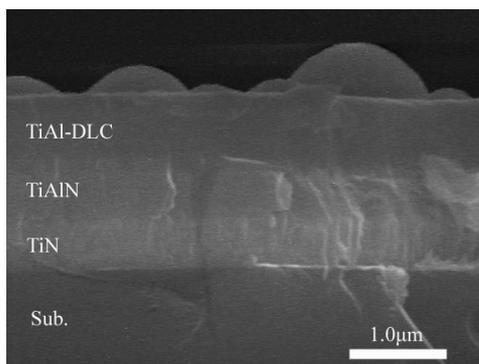


Fig. 2 A typical SEM cross-section micrograph showing the multilayered structure of TiAl-doped DLC/TiAlN/TiN film.

The Raman spectra of TiAl-doped DLC films deposited at various different parameters reveals similar profiles that the spectra consist of a broad peak at about  $1350\text{ cm}^{-1}$  and a peak at  $1550\text{ cm}^{-1}$ . The Raman intensity ratio  $I_D/I_G$ , was calculated by fitting two Gaussian curves and a linear background between  $900\text{ cm}^{-1}$  and  $1700\text{ cm}^{-1}$ . The  $I_D/I_G$  ratio obtained from the characteristic Raman G and D bands of TiAl-doped DLC specimens in terms of various bias voltages and  $\text{C}_2\text{H}_2$  partial pressures are identified as shown in Fig. 3 and Fig. 4. It is

well known that the Raman spectrum monitors the state of the  $\text{sp}^2$ -bond and  $\text{sp}^3$ -bond graphite structure [15, 16]. Most of the carbon atoms in DLC film form a  $\text{sp}^3$ -bond matrix and the remainders are  $\text{sp}^2$  sites. See Fig. 3, the intensity ratio of  $I_D/I_G$  decrease to the lowest value as the bias voltage increase from  $-50\text{ V}$  to  $-120\text{ V}$ , and then reverse to higher ratio as the bias voltage increase further. On the contrary, the microhardness of DLC films relatively increases with the increase of bias voltage from  $-50\text{ V}$  to  $-120\text{ V}$ , and then turn to decrease as the bias voltage increase further. On the other hand, see Fig. 4, the intensity ratio of  $I_D/I_G$  increase as  $\text{C}_2\text{H}_2$  partial pressures increase from  $2.0\text{ Pa}$  to  $3.3\text{ Pa}$ . The strong dependence of the properties of TiAl-doped DLC on the Raman spectra and microhardness indicates that bias voltage and  $\text{C}_2\text{H}_2$  partial pressures play a critical role in the deposition of TiAl-doped DLC. Similar parameter effects on the amorphous carbon films prepared by other PVD and CVD processes were reported [14, 17, 18]. In this study, the increase of  $I_D/I_G$  related to the progressive graphitization process in the film confirmed the trend of microhardness [14-16, 19]. Such an increase of  $I_D/I_G$  ratio means the increase of graphite microcrystallites in their volume. Therefore, it is assumed that the graphitization of the films starts from the applied bias voltages over  $-120\text{ V}$ . From the results, it revealed that the decrease of microhardness

of DLC films resulting from the graphitization with arriving carbon species at higher

bias voltage and higher  $C_2H_2$  partial pressures.

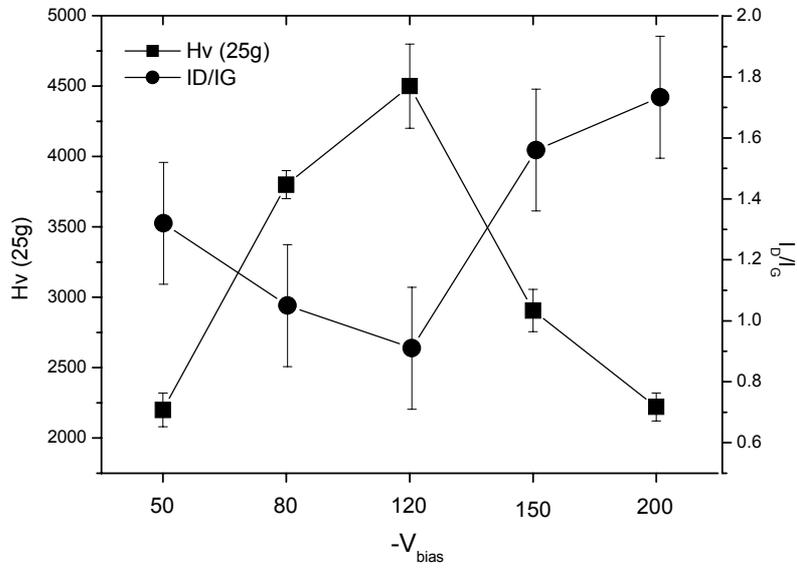


Fig. 3 Comparison of microhardness and Raman measured  $I_D/I_G$  ratio of TiAl-doped DLC films at different bias voltages.

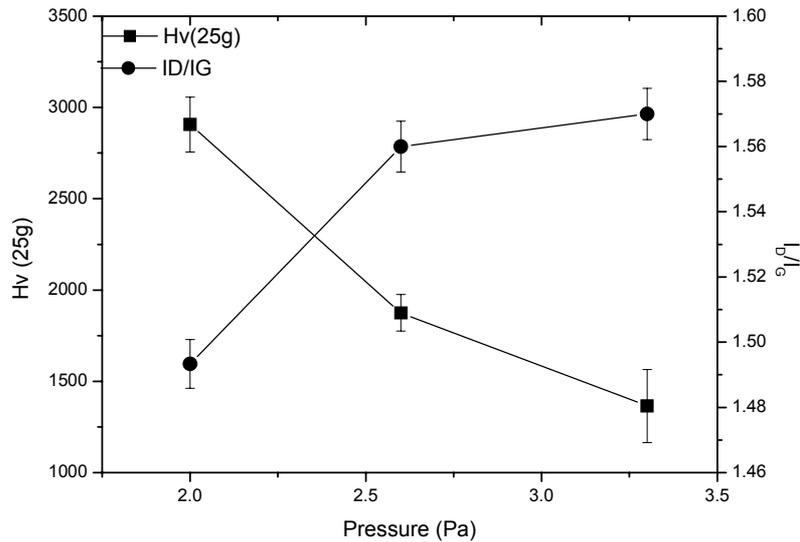


Fig. 4 Comparison of microhardness and Raman measured  $ID/IG$  ratio of TiAl-doped DLC films at different  $C_2H_2$  partial pressures

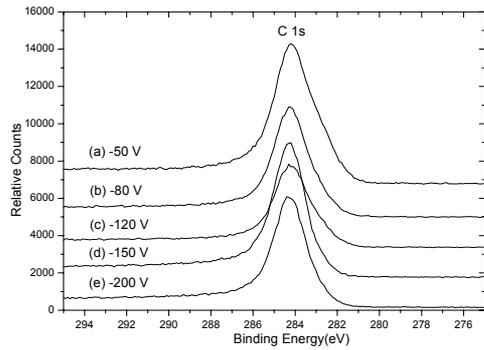
### 3.2 XPS analysis

The chemical state of carbon, titanium and aluminum in the films was analyzed by XPS, yielding C 1s, Ti 2p and Al 2p spectra for all specimens, as shown in Fig. 5 and Fig. 6. The XPS spectra of C 1s indicate that carbon was shifted to bonding energy of 284.2 eV as the bias voltage increased to -200 V or the C<sub>2</sub>H<sub>2</sub> partial pressures increased to 3.3 Pa, as shown in Fig. 5-(a) and Fig. 6-(a), relatively. As discussed in previous section, TiAl metals are in the form of small nanocrystallites of pure metal or metal carbides dispersed throughout the carbon network. The carbides exist at bonding energy of 455.5 eV and 72.7 eV [20-25], respectively. The XPS spectra of Ti 2p and Al 2p indicate that the titanium and aluminum intensity decreased with the increase of bias voltages and C<sub>2</sub>H<sub>2</sub> partial pressures, as shown in Fig. 5-(b) (c) and Fig. 6-(b) (c). Increasing the bias voltages or C<sub>2</sub>H<sub>2</sub> partial pressures, C-C bonds become more distinct in the spectrum. These results imply that the carbon bonding within the DLC films is not carbide bonding, and more graphite is present due to the decomposition of C<sub>2</sub>H<sub>2</sub> gas. This suggests that the graphitic structure was dominated in the film as the bias voltage or C<sub>2</sub>H<sub>2</sub> partial pressures increased.

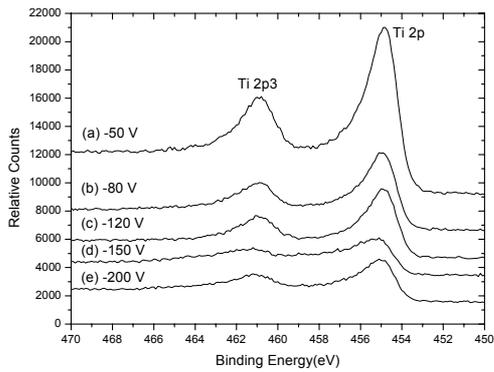
This result supports the Raman analysis.

Furthermore, decomposed XPS spectra of C 1s showed two types of bond including C-C (sp<sup>3</sup> bonds), C=C (sp<sup>2</sup> bonds). By fitting XPS C 1s core peak, Fig. 7 shows that the ratio of the fraction of sp<sup>3</sup> bonds to that of sp<sup>2</sup> bonds increases as the bias voltage increasing from -50 V to -120 V, and then turn into decreases with increasing bias voltages from -120 V to -200 V. Increase of bias voltage from -50 V to -120 V resulted in the formation of sp<sup>3</sup> microdomains in amorphous carbon network due to the accelerated positive ion bombardment of growing films. For negative bias greater than -120 V, the hardness of DLC film decreases sharply, since highly energetic ion bombardment by the excessive bias causes the transformation of sp<sup>3</sup> to sp<sup>2</sup>. On the other hand, Fig. 8 shows that the ratio of the fraction of sp<sup>3</sup> bonds to that of sp<sup>2</sup> bonds decreases as the C<sub>2</sub>H<sub>2</sub> partial pressures increasing from 2.0 Pa to 3.0 Pa, due to target poisoning lead to the smaller amounts of C<sub>2</sub>H<sub>2</sub> gas decomposed. The data presented in this figure extend the relationship between bias voltages and the sp<sup>3</sup> fraction or C<sub>2</sub>H<sub>2</sub> partial pressures and the sp<sup>3</sup> fraction that higher bias voltage or C<sub>2</sub>H<sub>2</sub> partial pressure corresponds to a lower sp<sup>3</sup> fraction.

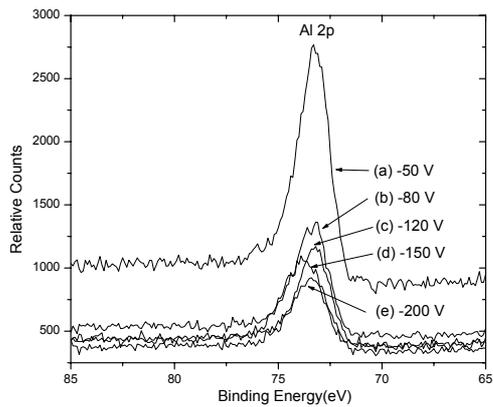
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(a)

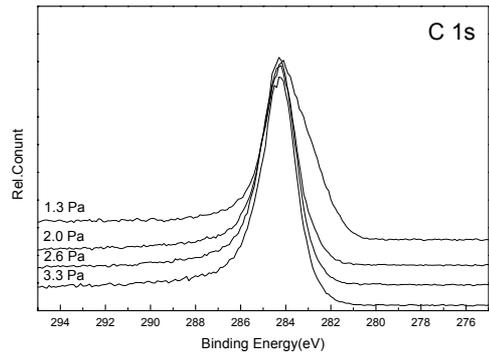


(b)

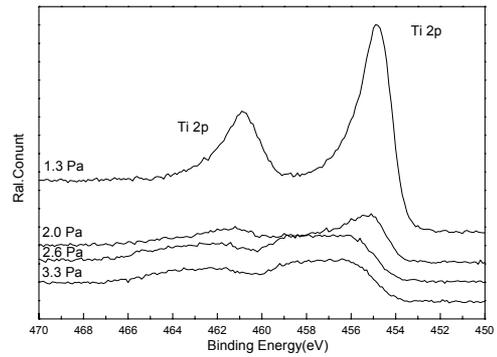


(c)

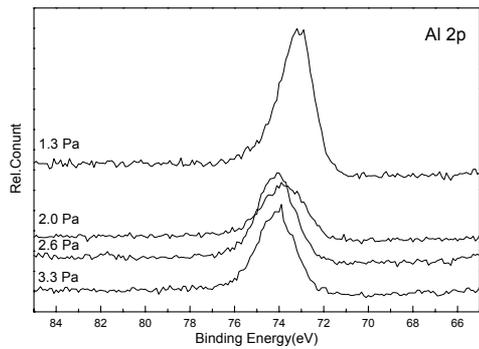
Fig. 5 XPS spectra of TiAl-doped DLC films at different bias voltages (a) C 1s, (b) Ti 2p, (c) Al 2p



(a)



(b)



(c)

Fig. 6 XPS spectra of TiAl-doped DLC films at different C<sub>2</sub>H<sub>2</sub> partial pressures (a) C 1s, (b) Ti 2p, (c) Al 2p

## Conclusions

The bias voltage and  $C_2H_2$  partial pressures play a major role in the microstructure change in the TiAl-doped DLC films. The profile of  $I_D/I_G$  ratio corresponds to the change of microhardness profile as the bias voltage or  $C_2H_2$  partial pressures varied. In this study ranges, higher bias voltage or higher  $C_2H_2$  partial pressure corresponds to a lower  $sp^3$  fraction, results in the lower microhardness of TiAl-doped

DLC coatings. In addition, TiAl metals are in the form of small nanocrystallites of pure metal or metal carbides dispersed throughout the carbon network.

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## References

- [1] H. Holleck, V. Schier, Surf. Coat. Technol., 76-77(1995) 328-336.
- [2] S. J. Bull, A. M. Jones, Surf. Coat. Technol., 78(1996) 173-184.
- [3] P. C. Yashar, W. D. Sproul, Vacuum 55(1999) 179-190.
- [4] M. Nordin, M. Larsson, S. Hogmark, Wear 232(1999) 221-225.
- [5] U. Wiklund, O. Wänstrand, M. Larsson, S. Hogmark, Wear 236(1999) 88-95.
- [6] E. Harry, M. Ignat, Y. Pauleau, A. Rouzaud, P. Juliet, Surf. Coat. Technol., 125(2000) 185-189.
- [7] M. S. Wong, G. Y. Hsiao, S. Y. Yang, Surf. Coat. Technol., 133-134(2000) 160-165.
- [8] J. Xu, K. Hattori, Y. Seino, I. Kojima, Thin Solid Films, 414(2002) 239-245.
- [9] B. Navinšek, P. Panjan, M. Čekada, D. T. Quinto, Surf. Coatings Technol., 154(2002) 194-203.
- [10] G. S. Shuster, G. K. Dosbaeva, Surf. Coatings Technol., 160(2002) 99-107.
- [11] V. Derflinger, H. Brändle, H. Zimmermann, Surf. Coatings Technol., 113(1999) 286-292.
- [12] C. L. Chang, W. Y. Ho, J. Y. Jao, T. C. Chang, D. Y. Wang, be presented the 1<sup>st</sup> International Conference on Advanced Tribology (I-CAT 2004), Paper No.: P-013.
- [13] Y.Y. Chang, D.Y. Wang, W.T. Wu, Thin Solid Films, 420-421 (2002) 241-247.
- [14] K.W. Wong, C.L. Chang, D.Y. Wang, Diamond Relat. Mater., 11 (7) (2002) 1447-1453.
- [15] J. Robertson, Materials Science and Engineering, R37 (2002) 129-281.
- [16] A.C. Ferrari and J. Robertson, Phys. Rev., B61 (2000) 14095-14107.
- [17] Yusuke Taki, Osamu Takai, Thin Solid Films 316 (1998) 45-50.
- [18] J. Robertson, Pure Appl. Chem., 66 (1994) 1789.
- [19] W.J. Yang, Y. Choa, T. Sekino, K. B. Shim, K. N. Niihara, K. H. Auh, Thin Solid Films 434 (2003) 49-54.
- [20] L.Zhang, R.V. Koka, Materials Chemistry and Physics 57 (1998) 23-32.
- [21] G. Soto, Applied Surface Science 233 (2004) 115-122.
- [22] Ding, Shi-Jin, Applied Surface Science 178 (1-4) (2001) 140-148.
- [23] S. Myhra, J.A.A. Crossley, M.W. Barsoum, Journal of Physics and Chemistry of Solids 62 (2001) 811-817.
- [24] P. Merel, M. Tabbal, M. Chaker, S. Moisa, J. Margot, Appl. Surf. Sci. 136 (1998) 105.
- [25] B.K. Tay, X. Shi, H.S. Tan, D.H.C. Chua, Surf. Interface Anal. 28 (1999) 231.