

General paper

Variation in Preferred Orientations of TiN Thin Films Prepared by Ion Beam Assisted Deposition

Akihito MATSUMURO*, Toshiyuki HAYASHI*, Mutsuo MURAMATSU*,
Yutaka TAKAHASHI**, Masao KOHZAKI* and Katsumi YAMAGUCHI*

*Department of Mechanical Engineering, Nagoya University,
Chikusa, Nagoya 464-8603, Japan

**Department of Mechanical Engineering, Mie University,
Kamihama, Tsu 514-8507, Japan

Abstract: The effects of various experimental conditions on the preferred orientations of titanium nitride (TiN) thin films were investigated. These films were formed on Si (100) wafers and sapphire (0001) substrates by ion beam assisted deposition (IBAD) with various N/Ti transport ratios, N ion incidence angles, film thicknesses and substrate temperatures. The acceleration voltage of the incident ions was 1 kV. The preferred orientation of the TiN films changed from (111) to (100) as the N/Ti transport ratios and ion incidence angles increased. This phenomenon is caused by the selective damage to crystal growth due to the energy of the bombarding particles. It was also found that an increase in film thickness changed the preferred orientation of the TiN (100) film to a (100) plus (110) orientation. Furthermore, this orientation reverted to (100) with the heating of the substrate during film preparation. It is concluded that these phenomena were caused by the process of minimizing the overall energy. Thus, the heating of the substrate was useful for synthesizing thick TiN (100) films in this preparation method. Transmission electron microscopy (TEM) observation of TiN (100) films suggested that these films had good crystallinity.

Key words: Titanium nitride, Preferred orientation, Ion beam assisted deposition, Transport ratio, Incidence angle, Thickness, Temperature

1. INTRODUCTION

TiN films are well known as wear- and corrosion-resistant films for use on mechanical components such as tool materials and bio-compatible materials. In recent years, much interest has been focused on TiN films as a diffusion barrier between Al wires and VLSI Si devices [1][2]. These TiN films have been synthesized by various physical and chemical deposition methods, such as ion plating [3], reactive sputtering [4], laser ablation and low-pressure chemical vapor deposition [5].

Recently, it has become necessary to control the preferred orientation of TiN thin films in order to investigate the anisotropy of their mechanical, physical and chemical properties. This knowledge will be indispensable for achieving preparations with excellent properties (e.g. high hardness, good wear- and corrosion- resistance). Accordingly, several studies on the control of the preferred orientation of TiN films have been carried out.

Oh and Je [6] suggested that the preferred orientation of TiN films formed by plasma-enhanced chemical vapor deposition (PECVD) and rf magnetron sputtering is determined by the level of minimization of the overall energy, which is the sum of surface free energy and strain energy. They reported that an increase in incident ion energy and in film thickness induced a change from (200) to (111) in the preferred orientation of TiN films. The effects of N₂ gas pressure on the preferred orientation

were also reported for reactive sputtering [7][8]. Ljungcrantz et al. [9] synthesized (001)-, (011)- and (111)-oriented TiN single crystals epitaxially on MgO substrates by dc magnetron sputtering. These epitaxial TiN crystals were considered suitable for studying the anisotropy of the mechanical and physical properties. However, such epitaxial films could be formed only on specific substrates. These films were prepared with low bombarding energies (i.e., 4.8×10^{-18} J (30 eV) or so at most) by sputtering. Therefore, it would seem that ion beam assisted deposition (IBAD) with higher bombarding energies is preferable in respect to adhesive properties and coating applications.

Kiuchi et al. [10] studied the control of the preferred orientation of TiN thin films produced by IBAD. They reported that the preferred orientation of TiN films with 30 kV ion acceleration changed from (111) to (200) with an increase in the N/Ti transport ratio. Bendavid et al. [11] investigated the preferred orientation of TiN thin films prepared by ion assisted arc deposition, and reported that the preferred orientation was influenced at the (220) orientation by increasing the ion acceleration voltage from 600 to 1200 V. In this study, however, the X-ray diffraction (XRD) pattern of (200)- and (220)- oriented TiN films showed one or two other peaks, respectively. Therefore, the control of the preferred orientation by IBAD has been received limited study, and must be explored further.

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We previously reported the effects of ion acceleration energy and N/Ti transport ratio on the phases, microstructures, hardness, elastic moduli, friction coefficients and adhesive strength of TiN films prepared by IBAD [12]. It was also reported that an ion acceleration voltage of 40 kV led to greater residual stress and poorer crystallization than with a voltage of 1 kV [12]. Accordingly, it is thought that control of the preferred orientation of TiN thin films must be studied with an N ion acceleration voltage of 1 kV, at which good crystallinity can be obtained.

In this study, TiN films were formed by IBAD with an N ion acceleration voltage of 1 kV. The effects of N/Ti transport ratio, N ion incidence angle, film thickness and substrate temperature on the preferred orientation were investigated. The mechanism which controls the preferred orientation of TiN thin films in this method was also considered. The crystallinity of the obtained TiN films was observed by transmission electron microscopy (TEM).

2. EXPERIMENTAL DETAILS

2.1. Preparation of TiN Films

TiN films were synthesized with evaporation of Ti by electron beams and simultaneous bombardment with N ion beams accelerated by 1 kV. Si (100) wafers were used as the substrate material for TiN formation. Sapphire (0001) substrates were also used in some experiments. The background pressure was 3.4×10^{-6} Pa and the operation pressure of the N₂ gas was 1.5×10^{-2} Pa. The ion beam flux was uniform at $37 \mu\text{A}/\text{cm}^2$ during all experiments, while the Ti deposition rates changed from 0.2 to 1.2 nm/s in order to vary the N/Ti transport ratios from 0.37 to 0.06. An N ion incidence angle of 0° was defined as the normal incidence on the substrate. The temperature of the substrate materials without Joule heating was below 100°C during deposition.

2.2. Film Characterization

The crystal structure and the preferred orientation were determined by XRD with Cu K α . The microstructure was observed through TEM images at an operation voltage of 300 kV. The content ratio (N/Ti) was analyzed by Auger electron spectroscopy (AES) with an operation voltage of 3 kV [13].

3. RESULTS AND DISCUSSION

3.1. Effect of N/Ti Transport Ratio on Preferred Orientation

The effect of the N/Ti transport ratio on the preferred orientation of TiN thin films was investigated under the experimental conditions shown in Table 1. These films were formed with a constant ion incident angle of 0°, film thickness of 200 nm and substrate temperature below

Table 1. Experimental conditions to evaluate of effect of N/Ti transport ratio on preferred orientation.

Sample no.	N/Ti transport ratio	N ion incidence angle °	Film thickness nm	Substrate temperature °C
1	0.37	0	200	< 100
2	0.19	0	200	< 100
3	0.09	0	200	< 100
4	0.06	0	200	< 100

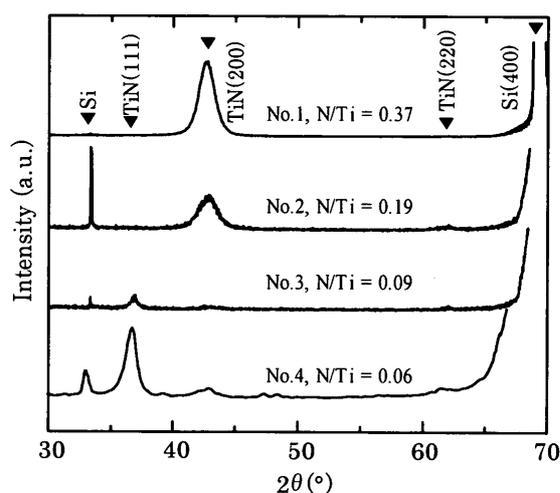


Fig. 1. XRD patterns of TiN thin films formed on Si with different N/Ti transport ratios. Experimental conditions for these samples are described in Table 1.

100°C. The N/Ti content ratio of these films was shown by AES analysis to be stoichiometric N/Ti = 1, despite their N/Ti transport ratio, owing to the chemical reaction between Ti and environmental N₂ gas. Figure 1 shows the XRD patterns as a function of the N/Ti transport ratio (sample no. 1-4). Owing to the change in Ti deposition rates from 0.2 to 1.2 nm/s, the N/Ti transport ratio decreased from 0.37 to 0.06. The preferred orientation of TiN films changed from (111) to (100) due to the increase of the N/Ti transport ratio. In the following, (111)- and (100)- oriented TiN thin films are referred to TiN (111) and TiN (100), respectively.

Kiuchi et al. [10] reported that TiN thin films prepared by dynamic ion mixing with an N ion incidence voltage of 30 kV changed from TiN (111) to TiN (200) as the N/Ti transport ratio increased from 6.5×10^{-3} to 0.03. The tendency which is illustrated in Fig. 1 therefore corresponds to this previous reports. However, well-oriented TiN (200) was not obtained, that is to say, one or two other peaks appeared [10]. Therefore, it is supposed that a bombarding voltage of 1 kV is favorable both in terms of the adhesive properties and in the controllability of the preferred orientation.

Turning now to the mechanism which controls the

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Table 2. Experimental conditions to evaluate of effect of N ion incidence angle on preferred orientation.

Sample no.	N/Ti transport ratio	N ion incidence angle °	Film thickness nm	Substrate temperature °C
1	0.37	0	200	< 100
5	0.37	18	200	< 100
6	0.37	45	200	< 100

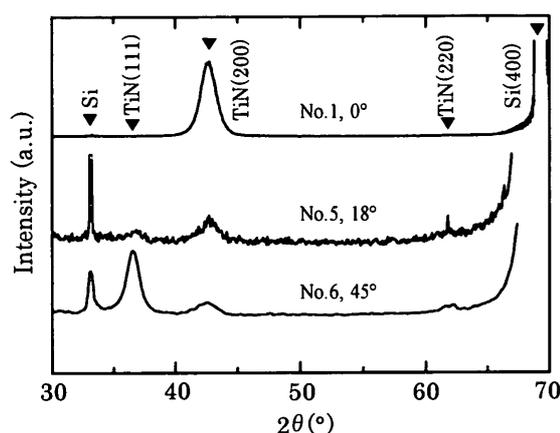


Fig. 2. XRD patterns of TiN thin films formed on Si substrate with different N ion incident angles. Experimental conditions for these samples are described in Table 2.

preferred orientation of TiN thin films, the mean free path of Ti vapor must be considered first. It is estimated that the mean free path of Ti vapor is about 2.5 m when the operation pressure of the N_2 gas is 1.5×10^{-2} Pa and the reaction occurs at room temperature. This value is sufficiently long in comparison with the distance between the substrate and the Ti evaporator (0.45 m). Therefore, the chemical reaction between Ti and N must be caused after arrival of the Ti vapor at the substrate. Thus, the preferred orientation of TiN films was determined by the arrangement of Ti atoms on the surface planes.

When there was no ion bombardment, the arrangement of Ti atoms grew preferentially on the (0001) plane of an h.c.p. system. With ion bombardment, growth on the (0001) plane was suppressed due to radiation damage, and thus occurred on the (10 $\bar{1}$ 0) plane [14]. Ti (0001) and (10 $\bar{1}$ 0) planes are structurally more closely related to the TiN (111) and (100) planes, respectively [14]. Therefore, it is considered that a low N/Ti transport ratio (sample no. 4: N/Ti = 0.06) induces the formation of TiN (111) due to the slight effects of the ion bombardment, and a high N/Ti transport ratio (sample no. 1: N/Ti = 0.37) induces the formation of TiN (100) due to the much larger effects of the nitrogen ion bombardment.

Table 3. Experimental conditions to evaluate of effect of film thickness on preferred orientation. The N/Ti transport ratio was kept at constant value of 0.37.

Sample no.	N/Ti transport ratio	N ion incidence angle °	Film thickness nm	Substrate temperature °C
1	0.37	0	200	< 100
7	0.37	0	500	< 100
8	0.37	0	1000	< 100

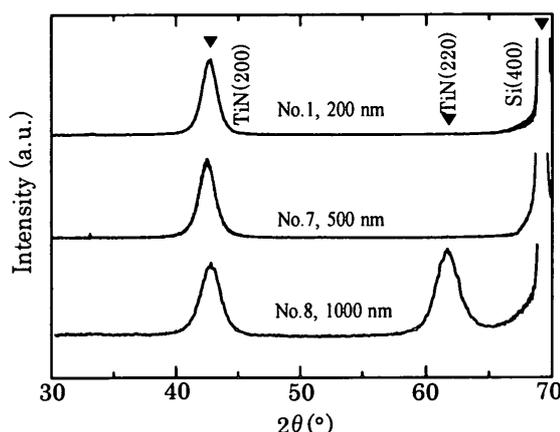


Fig. 3. XRD patterns of TiN thin films formed on Si substrate with different film thickness. Experimental conditions for these samples are described in Table 3.

3.2. Effect of Ion Incidence Angle on Preferred Orientation

The effect of the ion incidence angle on the preferred orientation of TiN thin films was investigated under the experimental conditions shown in Table 2. These films were formed with a constant N/Ti transport ratio of 0.37, film thickness of 200 nm and substrate temperature below 100°C. The N ion beam flux and Ti deposition rate were uniformly controlled regardless of changes in the ion incidence angle. Figure 2 shows the XRD patterns as a function of the N ion incidence angle (sample nos. 1, 5, 6). The preferred orientation of TiN thin films changed from (200) to (111) with increases in the incidence angle from 0° to 18° and 45°. This result is considered to be associated with the suppression of the selective radiation damage to Ti (0001), which is due to the decrease in the vertical momentum component of the bombarding particles corresponding to the increase in the ion incident angle.

3.3. Effect of Film Thickness on Preferred Orientation

The effect of the film thickness on the preferred orientation of TiN thin films was investigated with the two N/Ti transport ratios of 0.06 and 0.37.

First, the experiments were carried out with the N/Ti transport ratio of 0.37. The experimental conditions are shown in Table 3. These films were formed with a con-

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Table 4. Experimental conditions to evaluate of effect of film thickness on preferred orientation. The N/Ti transport ratio was kept at constant value of 0.06.

Sample no.	N/Ti transport ratio	N ion incidence angle °	Film thickness nm	Substrate temperature °C
4	0.06	0	200	< 100
9	0.06	0	500	< 100
10	0.06	0	1000	< 100

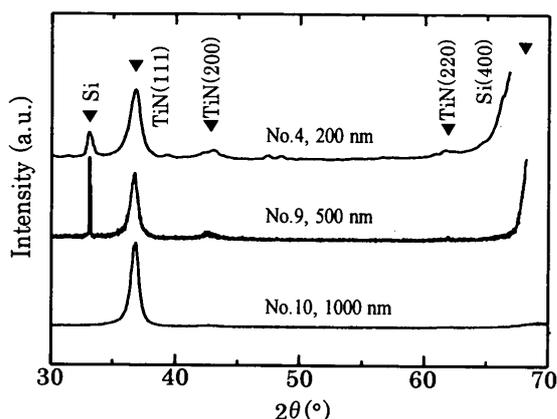


Fig. 4. XRD patterns of TiN thin films formed on Si substrate with different film thickness. Experimental conditions for these samples are described in Table 4.

stant N ion incidence angle of 0° and a substrate temperature below 100°C. Figure 3 shows the XRD patterns as a function of the film thickness (sample nos. 1, 7, 8). The preferred orientation of TiN thin films changed from (100) to (100) plus (110) with an increase in the film thickness from 200 nm to 1000 nm.

Next, the experiments were carried out with the N/Ti transport ratio of 0.06 and the other conditions shown in Table 4. Figure 4 shows the XRD patterns as a function of the film thickness (sample nos. 4, 9, 10). The preferred orientation of the TiN thin films showed no change despite the change in the film thickness.

On the other hand, Oh and Je [6] reported that the preferred orientation of TiN films formed by plasma-enhanced chemical vapor deposition (PECVD) and rf magnetron sputtering was determined by the level of minimization of the overall energy, which is the sum of surface free energy and strain energy, as shown in Fig. 5. However, the results shown in Fig. 3 cannot be explained by this finding.

It has been reported that the order of the surface free energy of TiN crystals is (111) > (110) > (100) [15]. For reasons mentioned above, the summation of surface free energy and strain energy was described as shown in Fig. 6. Without the selective radiation damaging of Ti (0001) due to N ion bombardment, the preferred orientation of TiN thin films changed from (100) to (111) when the film

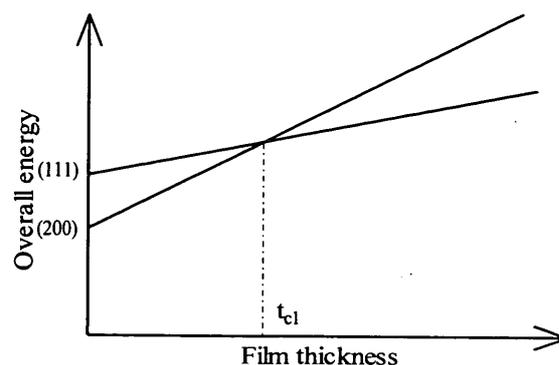


Fig. 5. Overall energy of TiN thin films with film thickness [6]. The overall energy consists of the surface energy and the strain energy.

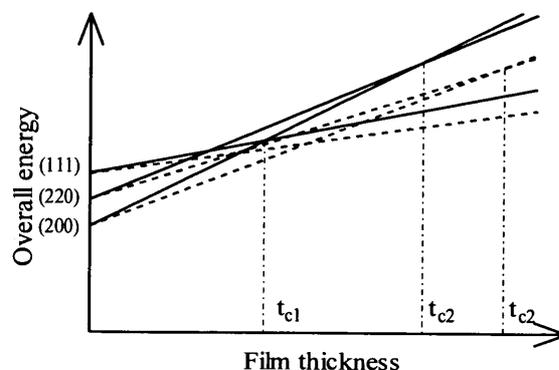


Fig. 6. Overall energy of TiN thin films with film thickness. Solid lines show the overall energy with no heating of the substrate, and broken lines show the overall energy with heating of the substrate.

thickness was over the threshold. With the suppression of Ti (0001) plane growth, competition for crystal growth occurred between the TiN (100) and TiN (110) planes. Because the intensity of TiN (100) and (110) peaks which appeared in the XRD pattern of sample 8 were almost equal, that the film thickness of sample 8 (1000 nm) is thought to correspond to the threshold indicated by the symbol t_{c2} in Fig. 6.

3.4. Effect of Substrate Temperature on Preferred Orientation

The effect of the substrate temperature on the preferred orientation of TiN thin films was investigated under the experimental conditions shown in Table 5. These films were formed with a constant ion incidence angle of 0°, N/Ti transport ratio of 0.37 and film thickness of 1000 nm. Figure 7 shows the XRD patterns as a function of the substrate temperature (sample nos. 8, 11, 12). The TiN thin films prepared with the substrate temperatures of 300 and 500 °C were strong-oriented TiN (100), while the film prepared at room temperature (below 100°C) was a (100) plus (110) oriented TiN thin film.

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Table 5. Experimental conditions to evaluate of substrate temperature on preferred orientation.

Sample no.	N/Ti transport ratio	N ion incidence angle °	Film thickness nm	Substrate temperature °C
8	0.37	0	1000	< 100
11	0.37	0	1000	300
12	0.37	0	1000	500

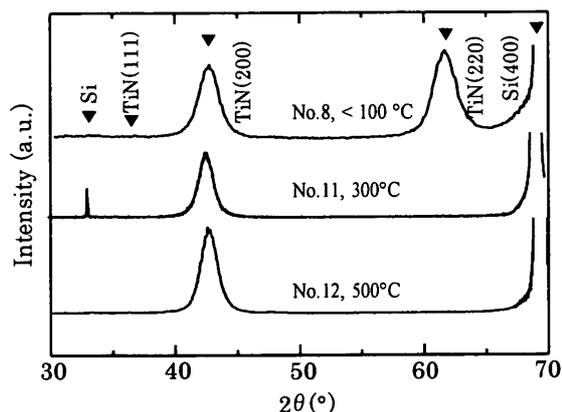


Fig. 7. XRD patterns of TiN thin films formed on Si substrate with different substrate temperatures. Experimental conditions for these samples are described in Table 5.

A relaxation of the strain energy was caused by the increase in substrate temperature during film formation. Therefore, the increases in the strain energy with and without heating of substrate may be described by the broken and solid lines in Fig. 6. Thus, the threshold thickness of the competitive relationship between TiN (200) and (220) crystal growth was increased from t_{c2} to t_{c2}' , shown in Fig. 6, by the heating of the substrate during film preparation. Accordingly, with substrate temperatures of 300 and 500°C, and the film thickness of t_{c2} , which corresponds to sample nos. 11 and 12 (1000 nm), the preferred orientation of TiN films was (100).

It follows from the above that the effects of the N/Ti transport ratio, N ion incidence angle, film thickness and substrate temperature on the preferred orientation of TiN thin films can be explained by the selective radiation damage to Ti (0001) caused by N ion bombardment and the minimization process of the overall energy.

In another part of the study, some TiN thin films were also formed on sapphire (0001) substrates. Figure 8 shows the XRD patterns of TiN thin films on sapphire (0001) substrate formed under the same conditions as used for sample nos. 10 and 12. These TiN films were both strong-oriented. This result proves that control of the preferred orientation is not limited to preparations on Si (100) substrates.

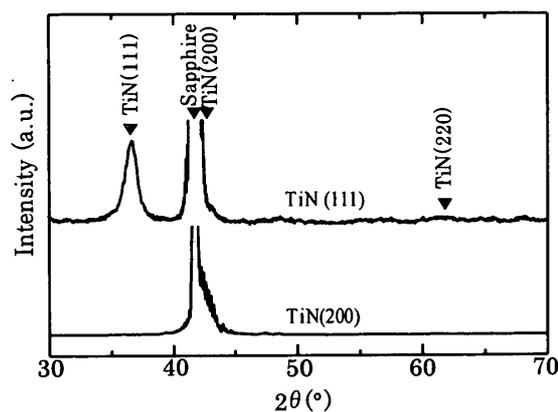


Fig. 8. XRD patterns of TiN thin films formed on sapphire substrate. TiN (111) and (200) were prepared under the same experimental conditions as sample nos. 10 and 12, respectively.

Unfortunately, well-oriented TiN (110) thin films were not synthesized in this study. There is room for further investigation of TiN (110) film formation.

3.5. Microstructure of Strong-oriented TiN Thin Films

Next, the microstructure of TiN thin films was investigated by TEM observation. Figure 9 shows a typical cross-sectional TEM observation of TiN (100) (sample no. 12) film. This image suggests that TiN film with good crystallinity was obtained, and also indicates that the spacing between TiN (100) planes was about 0.21 nm, which corresponds to the XRD pattern.

Based on the above, it is considered that strong-oriented TiN films with good crystallinity could be synthesized by ion beam assisted deposition with an N ion acceleration voltage of 1 kV.

4. CONCLUSIONS

In the present study, TiN thin films with preferred orientation were prepared by ion beam assisted deposition with an N ion acceleration voltage of 1 kV. The effects of the N/Ti transport ratio, N ion incidence angle, film thickness and substrate temperature on the preferred orientation was investigated.

- (1) The preferred orientation changed from (111) to (100) with an increase in N/Ti transport ratio from 0.06 to 0.37.
- (2) The preferred orientation changed from (100) to (111) with an increase in N ion incidence angle from 0° to 45°. It is considered that these phenomena were caused by the selective radiation damage to crystal growth due to the energy of the bombarding particles.
- (3) The preferred orientation of TiN films which was formed with the N/Ti transport ratio of 0.37 changed from

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Fig. 9. Typical cross-sectional TEM image of TiN film, corresponding to sample no. 12.

(100) to (100) plus (110) as the film thickness increased from 200 to 1000 nm, while the same increase in the film thickness did not influence the preferred orientation when the N/Ti transport ratio was 0.06.

(4) The preferred orientation changed from (100) plus (110) to (100) as the substrate was heated during film preparation. It is considered that this is caused by the process of minimizing the overall energy.

(5) Strong (111)- and (100)- oriented TiN films could be formed. With film thicknesses below 500 nm, control of the preferred orientation was achieved by controlling the N/Ti transport ratio. With a film thickness of 1000 nm, the heating of the substrate was also needed in order to

control the preferred orientation.

REFERENCES

- 1 T. Yamaguchi, T. Yamaoka, K. Yashiro and S. Sobue, *J. Appl. Phys.*, **78** (1995) 2385.
- 2 G. I. Grigorov, K. G. Grigorov, M. Stoyanova, J. L. Vignes, J. P. Langeron and P. Denjean, *Appl. Phys. A, Soli. Surf.*, **57** (1993) 195.
- 3 J. H. Givens and J. M. Rigsbee, *Surf. Coat. Technol.*, **54-55** (1992) 78.
- 4 I. Nishimura, T. Yuhta and T. Saitoh, *The Journal of the Surface Finishing Society of Japan*, **43** (1992) 78.
- 5 G. Reisse and R. Ebert, *Appl. Surf. Sci.*, **106** (1996) 268.
- 6 U. C. Oh and J. H. Je, *J. Appl. Phys.*, **74** (1993) 1692.
- 7 L. -J. Meng and M. P. d. Santos, *Surf. Coat. Technol.*, **90** (1997) 64.
- 8 H. H. Yang, J. H. Je and K. -B. Lee, *J. Mater. Sci. Lett.*, **14** (1995) 1635.
- 9 H. Ljungcrantz, M. Odén, L. Hultman, J. E. Greene and J. -E. Sundgren, *J. Appl. Phys.*, **80** (1996) 6725.
- 10 M. Kiuchi, A. Chayahara, Y. Horino, K. Fujii, M. Satou and W. Ensinger, *Appl. Surf. Sci.*, **60-61** (1992) 760.
- 11 A. Bendavid, P. J. Martin, X. Wang, M. Wittling and T. J. Kinder, *J. Vac. Sci. Technol., A* **13** (1995) 1658.
- 12 T. Hayashi, A. Matsumuro, M. Muramatsu, Y. Takahashi and K. Yamaguchi, *Thin Solid Films*, **349** (1999) 199.
- 13 D. G. Watson and W. F. Stickle, *Thin Solid Films*, **193/194** (1990) 305.
- 14 W. Ensinger, *Nucl. Instr. and Meth. in Phys. Res. B*, **127/128** (1997) 796.
- 15 J. Pelleg, L. Z. Zevin and S. Lungo, *Thin Solid Films*, **197** (1991) 117.