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Characterization and properties Ti–Al–Si–N nanocomposite coatings prepared by middle frequency magnetron sputtering

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ABSTRACT

TiN-containing amorphous Ti–Al–Si–N (nc–TiN/a–Si₃N₄ or a–AlN) nanocomposite coatings were deposited by using a modified closed field twin unbalanced magnetron sputtering system which is arc assisted and consists of two circles of targets, at a substrate temperature of 300 °C. XRD, XPS and High-resolution TEM experiments showed that the coatings contain TiN nanocrystals embedded in the amorphous Si₃N₄ or AlN matrix. The coatings exhibit good mechanical properties that are greatly influenced by the Si contents. The hardness of the Ti–Al–Si–N coatings deposited at Si targets currents of 5, 8, 10, and 12 A were 45, 47, 54 and 46 GPa, respectively. The high hardness of the deposited Ti–Al–Si–N coatings may be own to the plastic distortion and dislocation blocking by the nanocrystalline structure. On the other hand, the friction coefficient decreases monotonously with increasing Si contents. This result would be caused by tribo-chemical reactions, which often take place in many ceramics, e.g. Si₃N₄ reacts with H₂O to produce SiO₂ or Si(OH)₂ tribolay-layer.

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1. Introduction

The development and application of TiAlN coatings to cutting tools has led to dramatically extended tool life and the realization of high speed machining of hardened materials [1,2]. These coatings showed superior stability even at much elevated temperatures of approximately 800 °C [3,4]. The improved mechanical and oxidation properties were derived from the microstructure characterized by solid solution of Al into TiN [5,6]. However, Ti-Si-N coatings also attract large concerns with respect to hardness because the coating layers exhibit super hardness above 50 GPa [7,8]. The hardness of the Ti-Si-N coatings is known to come from nanocomposite characteristics of nc-TiN/a-Si₃N₄ [9,10]. Nanoscale crystallites TiN are relatively free of dislocations and when high stress is applied any dislocation movement that may be present is trapped at the grain boundaries by the amorphous matrix Si₃N₄ resulting in an enhancement in the material strength [11]. It has been suggested that the solid solution hardening may be the main reason responsible for the hardening of Ti-Al-N, while the grain boundary hardening may play a crucial in the hardening of Ti–Si–N [12]. Therefore, one could assume that if Ti-Al-N and Ti-Si-N were mixed together, formed quaternary nitrides might simultaneously have the unique properties of both two ternary composite coatings.

Up-to-date, Ti–Al–Si–N coatings have been developed by variety of deposition methods, such as plasma enhanced chemical vapor deposition (PECVD) [13], arc ion plating and sputtering [2], RF and DC reactive magnetron sputtering [12,14]. The vacuum arc process is an attractive production deposition technology but the requirement of silicon in the deposited nanocomposite coatings and the difficulty in arc-evaporating elemental Si has necessitated the use of special Me–Si alloy cathodes [15]. Alternatively, the silicon may be introduced into the coatings by concurrent operation of a titanium arc source and magnetron source operating with a silicon cathode. This approach has been successful both by simultaneous deposition of the two fluxes and by alternating arc and magnetron deposition [16,17].

To realize large-scale deposition with high uniformity of Ti–Al–Si–N coatings on random-shape machining tools and moulds, it is necessary to maintain a high plasma density in the deposition chamber. In this article, we present a design of a modified MF sputtering system and properties of Ti–Al–Si–N coatings deposited by using this system.

2. Experimental details

2.1. Deposition of coatings

The Ti–Al–Si–N nanocomposite coatings were deposited by using a modified closed field twin unbalanced magnetron sputtering system which is arc assisted and consists of two circles of

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targets, with a dimension of \emptyset 1000 mm \times 1000 mm, as shown in Fig. 1. The four targets are placed vertically on the sidewalls of the deposition chamber. The magnets of these four targets were placed behind the targets and the magnet arrangement of the four targets forms a closed magnetic field. In such magnetic field configuration the plasma is tightly confined between the four targets, resulting in a high plasma density in the chamber. A twin-purpose Ti₃Al cathode was designed, which either can be run in arc or magnetron sputtering mode. The substrates were placed vertically on a rotating sample carrier which was in between the targets. The targets were powered with bipolar 40 kHz power supplies. The samples spun in addition to rotation, and the base pressure prior to coating deposition was 5×10^{-3} Pa. During deposition, the substrates rotated in the deposition chamber and faced two Ti₃Al targets (99.99%) and two Si targets (99.99%) sequentially. The pulsed substrate bias was fixed at -75 V to optimize the deposition condition and the output current of the Ti₃Al targets was fixed at 100 A, while the output power to the Si paired targets was varied from 1.5 to 10 kW in order to prepare Ti-Al-Si-N coatings with different Si concentration. The mirror-polished stainless steel and Si (111) wafers were used as substrates and the coating process consisted of a 15 min deposition of a pure TiAl layer and a 60 min deposition of Ti-Al-Si-N layer. Typical deposition conditions for Ti–Al–Si–N coatings are 1:1 N₂/Ar ratio, 0.4 Pa total gas pressure, and 300 °C substrates temperatures. The Si targets current was varied at a time and then the changes in the resulting coatings were investigated.

2.2. Coating characterization

The surface morphologies of the Ti–Al–Si–N coatings were measured on a SHIMADZU SPM-9500J3 atomic force microscope (AFM). The Ti, Si and Al atomic concentration was determined by using an EDAX genesis 7000 EDS system operated at 25 kV. The chemical bonding was investigated by a Kratos 2AXIS2HS XPS system using Mg K_{α} (1253.6 eV) X-ray radiation. The microstructure measurements of coatings were carried out on JEM-2010FEF (UHR) transmission electron microscopes (TEM) operated at 200 kV. The hardness of the coatings was measured with a fully calibrated MTS Nano Indenter XP. The depth of indentation was set at 200 nm to avoid surface and substrate effect. On each sample, ten indentations were made at random locations and ten hardness values calculated for an average. An MS-T 3000 ball-on-disc tester was used for the



Fig. 1. Schematic diagram of the arc assisted middle-frequency magnetron sputtering system.

friction and wear measurements of the Ti–Al–Si–N nanocomposite coatings, which slide in ambient air at 23 °C and relative humidity (RH) 60%; a WC-Co ball with 6 mm in diameter was used as the mating material. A 5 N load was applied on the ball. The average sliding speed was 0.02 m/s for a fixed sliding time of 100 min. The friction coefficients of the coatings were continuously recorded during the test

3. Results and discussions

Fig. 2 showed the XRD patterns of Ti-Al-Si-N coatings deposited at Si targets currents of 5, 8, 10 and 12 A, respectively. It was found that all the as-deposited Ti-Al-Si-N coatings had a polycrystalline structure with multiple crystal planes orientations of (111), (200), (220), (311) and (222), respectively. The preferential (111) peak broadened with increasing Si targets currents. The peak broadening behavior was usually originated from the diminution of grain size [18] and the existence of residual stress induced in the crystal lattice [19]. No reflection peaks assigned to Si₃N₄ or AlN phases was observed. It was suggested that silicon may exist as an amorphous silicon nitride. The TiN crystallite sizes were calculated from (111) and (222) diffraction by using Scherrer formula by assuming the shape factor of 1 [20] and found to be between 8 and 11 nm. Also, Ti-Al-N solid solution in which Al atoms were substituted for Ti sites in TiN crystal may be formed [21]. A clear shift in the (111) peaks to lower angles was observed at higher concentrations of Si, which indicates an increase in the lattice constant. Si incorporation beyond 6 at.% into Ti-Al-N film would cause Si coprecipitation with (Ti, Al, Si)N crystallites from the vapor phase and the Si precipitates must be amorphous silicon nitride because they were formed under nitrogen plasma in low temperature PVD process as reported in the Ti-Si-N system [22]. Once the silicon nitride phase was formed, it would draw Si atoms from surroundings such as crystal surfaces of (Ti, Al, Si)N in order to grow itself.

Fig. 3a showed Si, Al and Ti contents in the Ti–Al–Si–N coatings as a function of MF sputtering current at a fixed Ti₃Al arc current of 100 A. The Si contents in the Ti–Al–Si–N coatings linearly increased from 2.2 to 8.4 at.% raising the sputter current from 5 to 12 A. This result reflected that our modified closed field twin unbalanced magnetron sputtering system enabled an easy control of Si content for the syntheses of Ti–Al–Si–N coatings. Because of detect limitation of EDS for light elements, more accurate experiments such as RBS are under way. Fig. 3b and c showed cross-sectional



Fig. 2. XRD patterns of Ti–Al–Si–N coatings deposited at Si targets currents of 5, 8, 10 and 12 A, respectively.



Fig. 3. Si, Al, and Ti contents in Ti–Al–Si–N coatings deposited at Si targets currents of 5, 8, 10 and 12 A, respectively (a). Cross-sectional SEM images of Ti–Al–Si–N coatings deposited at Si targets currents of 10 and 12 A are shown in b and c, respectively.

micrographs for Ti–Al–Si–N coatings deposited at Si targets currents of 10 and 12 A, respectively. The thickness of the coatings was about 2.5 μ m. Columnar structure was clearly seen in the coatings and the Ti–Al–Si–N coatings revealed a dense nanostructure. It was found that the Si addition into TiN coatings affected its microstructure to become finer in grain size and more random oriented in crystallographic direction [23,24].

XPS was performed to investigate the bonding status in the Ti–Al–Si–N coatings deposited at various Si targets currents and illustrated in Fig. 4. Bonding status of Ti was investigated and shown in Fig. 4a), peaks with binding energy of 455.5 and 458.4 eV were assigned to Ti $2p_{3/2}$ stoichiometric TiN and TiO_X, respectively [24]. So, the surface of the Ti–Al–Si–N coatings has been oxidized. Si 2p peak with a binding energy of 102.2 eV was obtained and shown in



Fig. 4. XPS spectra of Ti-Al-Si-N coatings deposited at Si targets currents of 5 and 10 A, respectively. (a) Ti 2p, (b) Si 2p, (c) N 1s, (d) Al 2 p.



Fig. 5. RMS roughness of Ti–Al–Si–N coatings deposited at Si targets currents of 5, 8, 10 and 12 A, respectively. Corresponding 2D and 3D AFM images of Ti–Al–Si–N coatings deposited at Si targets of 12 A are shown in the inset.

Fig. 4b). Peak position of Si 2p located at binding energy of 101.8 eV corresponding to N–Si bond of α -Si₃N₄ have been reported in previous literatures [25,26], which agreed well with the result of this study. The Si 2p peak intensity gradually increased with an increase of Si targets currents from 5 to 10 A. The N 1s spectrum (Fig. 4c) of the deposited Ti–Al–Si–N coating revealed typical features of TiN and Si₃N₄ with binding energies at 396.2 and 398.0 eV, respectively. The Al 2p peak located at 73.8 eV, was consistent with AlN. From XPS measurement and combined with our XRD results with no Si₃N₄ or AlN diffraction peaks, we concluded that Si₃N₄ was amorphous phase and Ti–Al–Si–N coatings existed as nc–TiN/a–Si₃N₄ or a–AlN.

The nanocomposite structure was obtained directly from TEM technique. A typical TEM image and selected area electron diffraction (SAED) pattern of the Ti-Al-Si-N coatings deposited at Si targets currents of 10 A were shown in Fig. 5. The mean crystallite size was about 8-10 nm which in good agreement with our result obtained by XRD using Scherrer's formula [27]. TiN crystallites were clearly distinguished from amorphous Si₃N₄ matrix by the lattice fringe contrast, and finely embedded in amorphous Si₃N₄ matrix and randomly distributed across the whole region. The diffraction ring was originated from the crystallite TiN crystallites. The reason for formation of such a nc-TiN/a-Si₃N₄ nanocomposite has been reported [28]. TiN phase can grow in high crystallinity at low temperature with the help of plasma energy. Nevertheless, Si_3N_4 crystallization required much high temperature due to high viscosity, so it was amorphous under the same experimental conditions [28]. Therefore, the structure of TiN crystallites embedded in an amorphous Si₃N₄ matrix can be easily obtained using solid state target under mild synthesis conditions. In such nanocomposite structure, TiN crystallites would be almost ideally interconnected via the structurally flexible and strong Si₃N₄ or AlN matrix which can accommodate the coherency strain.

AFM was used to investigate the effect of Si contents on the surface roughness of the Ti–Al–Si–N coatings and shown in Fig. 6. The surface become smoother and the root-mean-square (RMS) are gradually eliminated with increasing Si contents in the Ti–Al–Si–N coatings. The RMS values of Ti–Al–Si–N coatings deposited at Si targets currents of 5, 8, 10, and 12 A were 8.85, 7.95, 6.73 and 5.57 nm, respectively. No obvious microparticles are observed and the coatings were grown with dense and fine microstructure when the Si content in the coatings was increased.

The hardness of the Ti–Al–Si–N coatings was measured by nanoindentation and shown in Fig. 7. It is evident that the hardness is as a function of the Si contents and the maximum hardness was found for Ti–Al–Si–N coatings deposited at Si targets currents of 10 A. The hardness of the Ti–Al–Si–N coatings deposited at Si targets currents of 5, 8, 10, and 12 A were 45, 47, 54 and 46 GPa, respectively. The grain size (*D*) dependence of hardness or strength has been interpreted in terms of the Hall–Petch relationship [29]. According to this relation, the strength or hardness of polycrystalline material is often fit to a term proportional to $D^{-1/2}$. This result is related with the critical stress that is needed for the multiplication and movement of dislocations. This critical stress is inversely proportional to the distance between its pinning points [30], which will be limited by the grain size according with $\tau \approx Gb/D$. G is the shear modulus approximated by the function on the Young's modulus (*E*) and Poisson ratio (ν), $G = E(2 + 2\nu)^{-1}$, and *b* is the Burgers vector of the dislocation which defines the magnitude and direction of the slip [31]. This suggests that dislocation multiplication in nanophase materials will become increasingly difficult as the grain size decreases, because the so called Frank-Read sources cannot operate with in the small grains [32]. At sufficiently small grain size, the critical stress will eventually become larger than the yield stress in the conventional material. However, if the grain size is further reduced down to the nanometer range, the Hall-Petch relation loses validity and a softening is observed due to grain boundary sliding that become the most effective mechanism of stress relaxation [33].

Fig. 7b showed H^3/E^{*2} value of Ti–Al–Si–N coatings as a function of Si targets currents. The effective Young's modulus, $E^* = E/(1 - \nu^2)$ and H^3/E^{*2} value were calculated with the assumption of Poisson ratio, $\nu = 0.25$. The H^3/E^{*2} value is known to be proportional to the resistance to plastic deformation of hard materials. The highest H^3/E^{*2} value was obtained from the Ti–Al–Si–N coating having Si contents of 7 at.% and this coating would be most resistant to plastic deformation. The highest resistance to plastic deformation of that coatings would be related with hindering dislocation formation or movement due to nano-sized (Ti, Al, Si)N crystallites and



Fig. 6. TEM (a) and SAED (b) images of Ti-Al-Si-N coatings deposited at Si targets currents of 10 A.



Fig. 7. Hardness, Young's modulus (a) and H³/E⁺² values (b) of Ti-Al-Si-N coatings deposited at Si targets currents of 5, 8, 10 and 12 A, respectively.

the strong inhibiting of the crack propagation in amorphous Si_3N_4 or AlN. Similar results have been reported by Park [34].

The friction coefficient of the Ti–Al–Si–N coatings deposited at various Si targets currents are shown in Fig. 8. The friction coefficient of coatings deposited at 5, 8, 10 and 12 A were 0.85, 0.76, 0.75 and 0.69, respectively. This result would be caused by tribochemical reactions, which often take place in many ceramics, e.g. Si_3N_4 reacts with H_2O to produce SiO_2 or $Si(OH)_2$ tribolay-layer [35]. These products of SiO_2 and $Si(OH)_2$ were known to play a role as a self-lubricating layer and the formation of the tribo-layer would be more activated with increasing the Si content. Similar results have been reported by Park [23] and the friction coefficient was in the range of 0.6–0.9.

The hardness value of Ti–Al–Si–N coatings significantly increased up to 54 GPa for Ti–Al–Si–N coatings deposited at Si targets currents of 10 A compared with that of ~30 GPa for TiN coatings [37]. This surprising enhanced hardness is believed to originate from the microstructure evolution Ti–Al–N coatings with Si addition. Hardness enhancement upon energetic ion bombardment is frequently attributed to the induced compressive stress. However, when the compressive (or tensile) stress is induced in a bulk specimen by bending it, such an enhancement (or decrease) corresponds only to the amount of that stress because it is acting against the shear stress induced under the indenter by the applied load during the indentation hardness measurement. Therefore, a compressive stress alone can never enhance the hardness to 50–60 GPa. The high hardness of the deposited Ti–Al–Si–N coatings may be own to the plastic distortion [25] and dislocation



Fig. 8. Friction coefficient of Ti–Al–Si–N coatings deposited at Si targets currents of 5, 8, 10 and 12 A, respectively.

blocking by the nanocrystalline structure [36]. A nanocomposite structure with very fine crystallites resulted in the enhanced hardness of Ti-Al-Si-N coatings. In addition, grain boundary hardening derived from the increased cohesive energy at inter phase boundaries along with the percolation phenomenon of amorphous phase is believed to play a role in enhancing the hardness. The reasons for the large increases in hardness and Young's modulus of Ti-Al-N with Si addition would be the grain boundary hardening both by strong cohesive energy of interphase boundaries and by Hall-Petch relation derived from crystal size refinement [29], which were simultaneously caused by the percolation of amorphous Si₃N₄ into the Ti-Al-N coatings. Other possible reasons would be due to solid solution hardening of crystallites by Si dissolution into Ti-Al-N [30]. The maximum hardness value at the silicon content of approximately 7 at.% would result from the nanosized crystallites and their uniform distribution embedded in an amorphous Si₃N₄ matrix. Such a microstructure was in agreement with the concept of a nanocomposite, suggested by Veprek et al. [38,39]. However, the hardness reduction with further increases of Si content after maximum hardness has been explained with the thickening of amorphous Si₃N₄ phase with an increase of Si content. When amorphous Si₃N₄ are thickened, the ideal interaction between nanocrystallites and the amorphous phase is lost and the hardness of the nanocomposite becomes dependent on the property of the amorphous phase [38].

4. Conclusions

Nc–TiN/a–Si₃N₄ or a–AlN nanocomposite coatings were deposited by using a modified closed field twin unbalanced magnetron sputtering system which is arc assisted and consists of two circles of targets. The coatings exhibit good mechanical properties that are greatly influenced by Si contents in the Ti–Al–Si–N coatings. XPS, XRD and TEM showed that the coatings contain TiN nanocrystals embedded in the amorphous Si₃N₄ or AlN matrix. Coatings deposited at Si targets currents of 10 A exhibits excellent performance with a low friction coefficient of 0.72 and a high hardness of 54 GPa. These properties make it possible for industrial applications.

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References

- Y. Tanaka, N. Ichimiya, Y. Onishi, Y. Yamada, Surf. Coat. Technol. 146 (2001) 215.
- [2] S.G. Harris, E.D. Doyle, A.C. Vlasveld, P.J. Dolder, Surf. Coat. Technol. 146 (2001) 305.
- [3] D. Mcintyre, J.E. Greene, G. Hakansson, J.E. Sundgren, W.D. Munz, J. Appl. Phys. 67 (1990) 1542.
- [4] S. Paldey, S.C. Deevi, Mater. Sci. Eng. A 342 (2003) 58.
- [5] W.D. Munz, J. Vac. Sci. Technol. A 4 (6) (1986) 2717.
- [6] O. Knotek, M. Bohmer, T. Leyendeker, J. Vac. Sci. Technol. A 4 (6) (1986) 2695.
- [7] S. Veprek, H.D. Mannling, P. Karvankova, J. Prochazka, Surf. Coat. Technol. 200 (2006) 3876.
- [8] S. Veprek, S. Reiprich, L. Shizhi, Appl. Phys. Lett. 66 (1995) 2640.
- [9] S. Veprek, J. Vac. Sci. Technol. A 17 (5) (1999) 2401.
- [10] S. Veprek, M.G.J. Veprek-Heijman, P. Karvankova, J. Prochazka, Thin Solid Films 476 (2005) 1.
- [11] P.J. Martin, A. Bendavid, J.M. Cairney, M. Hoffman, Surf. Coat. Technol. 200 (2005) 2228.
- [12] N. Jiang, Y.G. Shen, H.J. Zhang, S.N. Bao, X.Y. Hou, Mater. Sci. Eng. B 135 (2006) 1.
- [13] P. Holubar, M. Jilek, M. Sima, Surf. Coat. Technol. 120 (1999) 184.
- S. Carvalho, E. Ribeiro, L. Rebouta, J. Pacaud, Ph. Goudeau, P.O. Renault, J.R. Riviere, Surf. Coat. Technol. 172 (2003) 109.
 C. D. Derschin, A.F. Gestere, A. Viene, A. Schutze, Cart.
- [15] O.D. Drouhin, A.E. Santana, A. Karimi, V.H. Derflinger, A. Schutze, Surf. Coat. Technol. 163 (2003) 260.
- [16] P.J. Martin, A. Bendavid, Thin Solid Films 394 (2001) 1.
- [17] O.N. Park, J.H. Park, S.Y. Yoon, M.H. Lee, K.H. Kim, Surf. Coat. Technol. 179 (2004) 83.
- [18] M. Diserens, J. Patscheider, F. Levy, Surf. Coat. Technol. 108–109 (1998) 241–246.
- [19] K.H. Kim, S.R. Choi, S.Y. Yoon, Surf. Coat. Technol. 298 (2002) 243.

- [20] D. Pilloudh, J.F. Pierson, P. Steyer, A. Mege, B. Stauder, P. Jacquot, Mater. Lett. 61 (2007) 2506.
- [21] J. Musil, H. Hruby, Thin Solid Films 365 (2000) 104.
- [22] S.H. Kim, J.K. Kim, K.H. Kim, Thin Solid Films 420 (2002) 360.
- [23] I.W. Park, S.R. Choi, J.H. Sub, C.G. Park, K.H. Kim, Thin Solid Films 447 (2004) 443.
- [24] C.W. Zou, H.J. Wang, M. Li, Y.F. Yu, C.S. Liu, L.P. Guo, D.J. Fu, Vacuum 84 (2010) 817.
- [25] M. Nose, Y. Deguchi, T. Mae, E. Honbo, T. Nagae, K. Nogi, Surf. Coat. Technol. 174 (2003) 261.
- [26] H. Du, R.E. Tressler, K.E. Spear, C.G. Pantano, J. Electrochem. Soc. 136 (1989) 1527.
- [27] S. Christiansen, M. Albrecht, H.P. Strunk, S. Veprek, J. Vac. Sci. Technol. B 16 (1) (1998) 19.
- [28] H.Y. Zhao, Q.L. Fan, L.X. Song, T. Zhang, E.W. Shi, X.F. Hu, Appl. Surf. Sci. 252 (2006) 3065.
- [29] C. Suryanarayana, D. Mukhopadhyay, S.N. Patankar, F.H. Froes, J. Mater. Res. 7 (1992) 2114.
- [30] S. Carvalho, L. Rebouta, A. Cavaleiro, L.A. Rocha, J. Gomes, E. Alves, Thin Solid Films 398 (2001) 391.
- [31] A.A. Voevodin, J.S. Zabinski, Thin Solid Films 370 (2000) 223.
- [32] J.S. Koehler, Phys. Rev. B 2 (1970) 223.
- [33] W.G. Nieman, J.R. Weerman, R.W.R.W. Siegll, J. Mater. Res. 6 (1991) 1012.
- [34] I.W. Park, S.R. Choi, J.H. Suh, C.G. Park, K.H. Kim, Thin Solid Films 447 (2004) 443.
- [35] M.P. Delplancke-Ogletree, O.R. Monteiro, Surf. Coat. Technol. 108 (1998) 484.
- [36] S. Zhang, D. Sun, Y.O. Fu, H.J. Du, Surf. Coat. Technol. 167 (2003) 113.
 [37] P. Steyer, A. Mege, D. Pech, C. Mendibide, J. Fontaine, J.F. Pierson, C. Esnouf, P.
- Goudeau, Surf. Coat. Technol. 202 (2008) 2268. [38] S. Veprek, P. Karvankova, M.G.J. Veprek-Heijman, J. Vac. Sci. Technol. B 23 (2005) 1.17.
- [39] S. Veprek, H.D. Mannling, A. Niederhofer, D. Ma, S. Mukherjee, J. Vac. Sci. Technol. B 22 (2004) L5.