

# Superhard nanocrystalline composite materials: The TiN/Si<sub>3</sub>N<sub>4</sub> system

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Thin films of novel superhard composite materials consisting of TiN nanocrystals in an amorphous Si<sub>3</sub>N<sub>4</sub> matrix have been prepared by means of plasma chemical vapor deposition. The films show a high Vickers hardness of 5000 kg/mm<sup>2</sup> and elastic modulus of >500 GPa, and they are resistant against oxidation in air up to ≥800 °C. The theoretical background of these unusual properties are briefly discussed and practical rules suggested according to which similar properties should be expected for composites of other ternary systems. © 1995 American Institute of Physics.

Mechanical properties of materials are determined by the formation and movement of dislocations and cracks.<sup>1-3</sup> The stress  $\sigma$  needed to move a dislocation which is pinned, e.g., by precipitates separated by a distance  $L$  is proportional to  $1/L$ .<sup>1,2</sup> Under applied stress a segment between the pinning points acts as a "Frank-Read" source for dislocation multiplication. The density of the dislocations created under a given applied stress can be related to the grain size of a polycrystalline material giving the Hall-Petch relationship between the cleavage strength  $\sigma_c$  and the average linear dimension of the grain  $l$ ,<sup>4,5</sup>  $\sigma_c = \sigma_0 + c \cdot l^{-1/2}$ . This relation has been experimentally verified for steel and zinc,<sup>5</sup> sintered alumina and many other materials<sup>2,6</sup> to apply for grain sizes of ≥5 μm. At a smaller grain size a saturation of the hardness has been observed and explained by a dislocation substructure.<sup>6,7</sup> Shih *et al.* found this relationship to apply down to a grain size of 0.05 μm for sputter deposited polycrystalline tungsten films<sup>8</sup> and for polycrystalline multilayers of Ti/TiN, Hf/HfN, and W/WN<sub>x</sub>.<sup>9</sup>

The dependence of the hardness and elastic modulus on the microstructure for smaller grain sizes has been studied on the polycrystalline metallic laminates<sup>10</sup> and epitaxially deposited heterostructures of TiN/VN,<sup>11</sup> TiN/V<sub>x</sub>Nb<sub>y</sub>N,<sup>12-14</sup> and TiN/NbN.<sup>15</sup> The largest enhancement of the hardness of such heterostructures is found for an optimum period of the heterostructure of 5–7 nm and explained mainly in terms of a theory published earlier by Koehler.<sup>16</sup> Accordingly, a strong enhancement of the strength should be expected in epitaxial heterostructures consisting of two metals  $A$  and  $B$  with a high and low dislocation line energy, respectively. The thickness of the layers should be small enough so that the Frank-Read source cannot operate. Thus, dislocations will form in the metal  $B$ . If the difference in the dislocation line energies of both metals is large enough, the dislocation in  $B$  will be prevented to cross the  $A/B$  interface under applied external stress which results in an increased strength of the layered structure as compared with the homogeneous alloy. Koehler's prediction has been verified experimentally on polycrystalline Cu/Al laminates with different periods ranging from 20 to 1000 nm.<sup>10</sup> For a thickness between 1000 and

70 nm the tensile fracture stress increased with decreasing thickness according to the Hall-Petch relationship. Below 70 nm a saturation was found with an enhancement of the strength by about a factor of 3 as compared to a homogeneous alloy. A later work on the epitaxial heterostructures TiN/NbN, TiN/VN, and TiN/V<sub>1-x</sub>Nb<sub>x</sub>N revealed another increase of the strength for an optimum value of the period of 4–10 nm followed by its decrease for smaller periods due to interdiffusion and mixing at the interface.<sup>15</sup> A discussion of the theoretical models which explain this large strength enhancement, such as supermodulus effect due to singularity in electronic band structure,<sup>17</sup> coherency strain effect at the interface<sup>15,18,19</sup> and the dislocation line energy effects is beyond the scope of this letter (see, e.g., Refs. 15,17–19,28).

Based on these theoretical considerations we expect that a strong enhancement of the hardness and elastic modulus should be found in nanocrystalline/amorphous ( $nc/a$ ) composites which show a large miscibility gap at sufficiently high temperatures. This provides sharp interfaces between the nanocrystals and amorphous matrix. Dislocations which might form in the crystallites cannot move through the amorphous matrix. Crystals of a few nanometers size are free of dislocations. The amorphous matrix has to have a high energy of crack formation and propagation at the temperatures at which the material will be exposed to the load. A subnanometer thin three-dimensional amorphous skeleton should show an enhanced strength against crack formation and propagation than bulk material. A randomly oriented nanocrystals embedded within a thin amorphous matrix provide a better coherence at the grain boundaries than purely polycrystalline composites, and they should be more suitable for applications as tribological coatings than the single- or polycrystalline multilayers mentioned above. In order to avoid the interdiffusion and to form sharp boundaries the preparation of the material should take place at a low temperature. Therefore, plasma chemical and physical vapor deposition, CVD and PVD, appears to be the most promising technique for these purposes. A controlled ion bombardment at low energies allows one to adjust the desirable crystallite size, mechanical stress, and avoid columnar structure in the films.<sup>20,21</sup>

A suitable system for the initial studies appeared to be the  $nc$ -TiN/ $a$ -Si<sub>3</sub>N<sub>4</sub> composite as it shows, even at high temperatures, a large miscibility gap.<sup>22</sup> Both titanium and silicon

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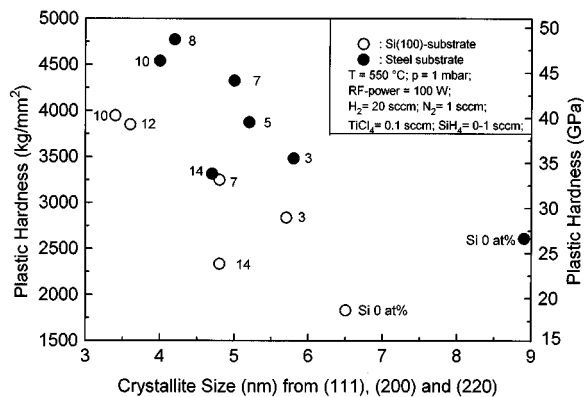


FIG. 1. Dependence of the hardness of *nc*-TiN/*a*-Si<sub>3</sub>N<sub>4</sub> composites on the crystallite size. Open symbols Si (100) substrate, full symbols stainless steel. The numbers next to the symbols indicate the silicon content in the films.  $T_{\text{dep}}=550\text{ }^{\circ}\text{C}$ , total pressure 1 mbar, rf power 100 W, gas flow rates: hydrogen 20 SCCM, nitrogen 1 SCCM, TiCl<sub>4</sub> 0.1 SCCM, SiH<sub>4</sub> 0.2–1 SCCM (varied).

nitrides are refractory materials with a high strength and hardness.<sup>3</sup> At a temperature of about 550 °C, TiN forms perfect nanocrystals whereas Si<sub>3</sub>N<sub>4</sub> is amorphous. We also expect that the silicon nitride will provide the composite material with a larger stability against oxidation than that which is found for metallic nitrides and comparable or even higher than Ti<sub>1-x</sub>Al<sub>x</sub>N.<sup>23–25</sup>

In an earlier paper one of the authors reported the plasma CVD of Ti<sub>1-x</sub>Si<sub>x</sub>N films from titanium and silicon chlorides in a dc glow discharge.<sup>26</sup> He has also found a strong increase in the Vicker's hardness of the films with a silicon content of ~10–12 at. %. In the present work we have used a mixture of SiH<sub>4</sub> and TiCl<sub>4</sub> diluted with hydrogen and nitrogen which assured a low chlorine content in the films. The deposition has been done in a rf discharge with a variable excitation frequency in order to control the self-bias independently of other discharge parameters.<sup>27</sup> The results to be reported here have been obtained at a frequency of about 15 MHz, total pressure of 1 mbar, and a substrate temperature of 550 °C. The silicon content in the films has been varied via the flow rate of silane. The deposition rate was about 0.8–0.9 nm/s independent of the silicon content. More details will be published elsewhere.<sup>28</sup>

Figure 1 shows the dependence of the plastic hardness<sup>29</sup> on the crystallite size, determined from the x-ray diffraction data,<sup>30</sup> for films deposited on steel and single crystalline silicon (100) substrates. The strong increase of the hardness with decreasing crystallite size down to 3 nm is clearly seen. The hardness of films deposited on steel reaches almost 5000 kg/mm<sup>2</sup> (50 GPa). The somewhat lower hardness of films deposited on silicon substrates is probably due to their lower surface temperature.<sup>28</sup> The smallest crystallite size and maximum hardness is reached at a silicon content in the films of about 8–9 at. %. The chlorine content of such films of ~0.2 at. % is much lower than in those deposited from SiCl<sub>4</sub> [ $\geq 2$  at. % (Ref. 26)]. The films consist of stoichiometric TiN and Si<sub>3</sub>N<sub>4</sub>.<sup>28</sup>

A high hardness alone is not a sufficient criterion for a suitability of the coatings for tribological applications. A

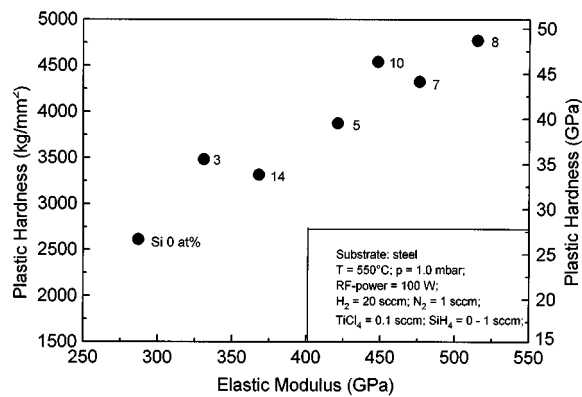


FIG. 2. Correlation of the hardness and elasticity modulus for *nc*-TiN/*a*-Si<sub>3</sub>N<sub>4</sub> composites with a various silicon content (indicated by the numbers next to the symbols) and crystallite size (see Fig. 1); substrate steel.

high stiffness and stability against oxidation is needed as well. Figure 2 shows the correlation between the hardness and the elastic modulus determined from the microindentation measurements.<sup>29</sup> These are the typical values from a series of measurements using increasing maximum load and indentation depth which eliminates the possible errors.<sup>31–35</sup> In view of the possible application of the coatings it is very encouraging to see that the increasing hardness is accompanied by an increase of the elastic modulus.

Figure 3 shows the weight increase of the films with a Si content of 7–9 at. % due to their oxidation in air. Unlike TiN films which already show strong oxidation at a temperature of 550 °C,<sup>23</sup> A significant oxidation of our composite commences only at about 850 °C.

The crystallite size, which determines the mechanical properties, reaches a minimum value of 3.0–3.5 nm at a silicon content of ~8–9 at. % where the hardness and elastic modulus reach maximum (Figs. 1 and 2). This minimum crystallite size is close to the value of the lower limit of the stability of crystalline silicon<sup>36</sup> and metallic heterolayers<sup>37</sup> below which a transition to amorphous phase occurs. It will be interesting to find out if a further decrease of the crystallite size of TiN below the present minimum value is possible, and if it will result in a further increase of the hardness and elastic modulus.

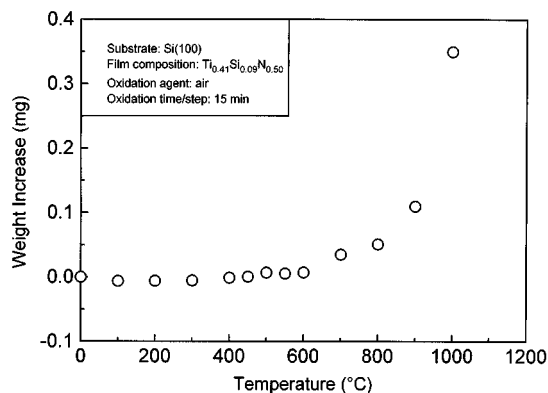


FIG. 3. Increase of the weight of the films due to their oxidation in air for 15 min at the given temperature; silicon substrate.

The silicon content also controls the strain in the TiN crystallites which reaches a maximum of about 1.2% at a Si content of ~7–8 at. %. It is not yet clear to what extent this strain can contribute to the enhanced hardness and elastic modulus. However, as it reaches only a relative shallow maximum at a Si content smaller than that needed for optimum hardness and elastic modulus, the observed strengthening is due primarily to the minimum crystallite size and thin Si<sub>3</sub>N<sub>4</sub> matrix. The hardness of 5000 kg/mm<sup>2</sup> is comparable to the maximum value found in the epitaxial TiN/NbN and TiN/VN heterostructures with a period of about 5 nm.<sup>15</sup> However, in the later case the hardness strongly decreased for heterostructures with a smaller period. Since no such decrease with crystallite size down to 3 nm occurs in our films we conclude that interdiffusion and mixing is much smaller during the plasma CVD at 550 °C than at the higher temperatures used for the deposition of the epitaxial heterostructures (typically ≥700 °C, e.g., Refs. 11, 13, and 15).

In conclusion, we have shown that thin films of a composite material consisting of nanocrystalline TiN and amorphous Si<sub>3</sub>N<sub>4</sub> reach a remarkably high hardness of 5000 kg/mm<sup>2</sup> (50 GPa) and elastic modulus of >500 GPa. The films are resistant against oxidation in air up to more than 800 °C. Their deposition by plasma CVD (or PVD) at a substrate temperature of 500 °C makes them suitable for many applications.

The principles for the design of such superhard and tough materials outlined above suggest that a large variety of composite materials using various refractory nanocrystallites in an amorphous matrix can be prepared in a similar way. Indeed, similar results have been achieved more recently in the nc-W<sub>2</sub>N/a-Si<sub>3</sub>N<sub>4</sub> composites.<sup>38</sup> The thermodynamical principles for the design of such materials will be discussed in a forthcoming paper.<sup>28</sup>

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<sup>1</sup>D. Hull, *Introduction to Dislocations* (Pergamon, Oxford, 1965).

<sup>2</sup>R. W. K. Honeycombe, *The Plastic Deformation of Metals*, 2nd ed. (Edward Arnold, London, 1984).

<sup>3</sup>A. Kelly and N. H. MacMillan, *Strong Solids*, 3rd ed. (Clarendon, Oxford, 1986).

<sup>4</sup>E. O. Hall, *Proc. Phys. Soc. London Sect. B* **64**, 747 (1951).

<sup>5</sup>N. J. Petch, *J. Iron Steel Inst.* **174**, 25 (1953).

<sup>6</sup>S. D. Skrovanek and R. C. Brandt, *J. Am. Ceram. Soc.* **62**, 215 (1979).

<sup>7</sup>D. Kuhlmann-Wilsdorf, *Trans. AIME* **224**, 1047 (1962); and *Metall. Trans.* **1**, 3173 (1970).

<sup>8</sup>K. K. Shih, D. A. Smith, and J. R. Crowe, *J. Vac. Sci. Technol. A* **6**, 1681 (1988).

<sup>9</sup>K. K. Shih and D. B. Dove, *Appl. Phys. Lett.* **61**, 654 (1992).

<sup>10</sup>S. L. Lehoczky, *J. Appl. Phys.* **49**, 5479 (1978).

<sup>11</sup>U. Helmersson, S. Todorova, S. A. Barnett, and J.-E. Sundgren, *J. Appl. Phys.* **62**, 481 (1987).

<sup>12</sup>P. B. Mirkarimi, L. Hultman, and S. A. Barnett, *Appl. Phys. Lett.* **57**, 2654 (1990).

<sup>13</sup>K. M. Hubbard, T. R. Jervis, P. B. Mirkarimi, and S. A. Barnett, *J. Appl. Phys.* **72**, 446 (1992).

<sup>14</sup>P. B. Mirkarimi, S. A. Barnett, K. M. Hubbard, T. R. Jervis, and L. Hultman, *J. Mater. Res.* **9**, 1456 (1994).

<sup>15</sup>M. Shinn, L. Hultman, and S. A. Barnett, *J. Mater. Res.* **7**, 901 (1992).

<sup>16</sup>J. S. Koehler, *Phys. Rev. B* **2**, 547 (1970).

<sup>17</sup>W. E. Pickett, *J. Phys. F* **12**, 2195 (1982).

<sup>18</sup>J. W. Cahn, *Acta Metall.* **11**, 1274 (1963).

<sup>19</sup>D. Wolf and J. F. Lutsko *Phys. Rev. Lett.* **60**, 1170 (1988).

<sup>20</sup>S. Veprek, *Proceedings of the European Material Research Society Symposium on Non-Crystall. Material*, Strasbourg, June 1984, edited by P. Pinard and S. Kalbitzer (Les Éditions de Physique, Les Ullis, France, 1984), p. 425.

<sup>21</sup>S. Veprek, F.-A. Sarott, and Z. Iqbal, *Phys. Rev. B* **36**, 3344 (1987).

<sup>22</sup>S. Sambasivan and W. T. Petuskey, *J. Mater. Res.* **9**, 2362 (1994).

<sup>23</sup>W.-D. Münz, *J. Vac. Sci. Technol. A* **4**, 2717 (1986).

<sup>24</sup>O. Knotek, M. Böhmer, and T. Leyendecker, *J. Vac. Sci. Technol. A* **4**, 2695 (1986).

<sup>25</sup>Y. Tanaka, T. M. Gür, M. Kelly, S. B. Hangstrom, T. Ikeda, K. Wakihira, and H. Satoh, *J. Vac. Sci. Technol. A* **10**, 1749 (1992).

<sup>26</sup>L. Shizi, S. Yulong, and P. Hongrui, *Plasma Chem. Plasma Process.* **12**, 287 (1992).

<sup>27</sup>S. Veprek, in *Proceedings International Summer School on Plasma Chemistry*, edited by S. Veprek and M. G. J. Veprek-Heijman (Tecm. Univ. Munich, Munich, 1991).

<sup>28</sup>S. Veprek and S. Reiprich, *Thin Solid Films* (in press).

<sup>29</sup>The measurements of the hardness and elastic modulus have been done with a computer controlled microindenter Fischerscope H 100 strictly following the procedure outlined in Refs. 31–35. In such a measurement one records the dependence of the indentation depth on the stepwise increased load until a sufficient amount of plastic deformation (≥0.2 μm) has been reached. The hardness is calculated from the depth of plastic deformation and the maximal load (typically 10–30 mN). The elastic modulus is calculated from the linear part of the unloading curve.

<sup>30</sup>H. P. Klug and L. E. Alexander, *X-Ray Diffraction Procedures*, 2nd ed. (Wiley, New York, 1974).

<sup>31</sup>H.-H. Behncke, *Härtereitechnische Mitteilungen* **48**, 3 (1993).

<sup>32</sup>H.-H. Behncke and W. Weiler, *Materialprüfung* **30**, 239 (1988).

<sup>33</sup>P. Neumaier, *Metalloberfläche* **2**, 41 (1989).

<sup>34</sup>T. F. Page, *J. Mater. Res.* **7**, 450 (1992).

<sup>35</sup>T. F. Page and S. V. Hainsworth, *Surf. Coat. Technol.* **61**, 201 (1993).

<sup>36</sup>S. Veprek, Z. Iqbal, and F.-A. Sarott, *Philos. Mag.* **B 45**, 137 (1982).

<sup>37</sup>M. R. Khan, C. S. L. Chun, G. P. Felcher, M. Grimsditch, A. Kueny, Ch. M. Falco, and I. K. Schuller, *Phys. Rev. B* **27**, 7186 (1983).

<sup>38</sup>S. Veprek, S. Reiprich, and M. Hausmann, *Materials Research Symposium Spring Meeting*, 16–21 April 1995 (in press).