



Experimental and theoretical studies of the physicochemical and mechanical properties of multi-layered TiN/SiC films: Temperature effects on the nanocomposite structure

Alexander D. Pogrebnyak^{a,*}, Volodymyr I. Ivashchenko^b, Petro L. Skrynskyi^b,
Oleksandr V. Bondar^a, Piotr Konarski^c, Karol Załęski^d, Stefan Jurga^{d,e}, Emerson Coy^{d,**}

^a Sumy State University, R.-Korsakova 2, 40007 Sumy, Ukraine

^b Frantsevych Institute for Problems of Material Science, NAS of Ukraine, 3, Krzhyzhanovskyy Str., 03142 Kyiv, Ukraine

^c Tele and Radio Research Institute, ul. Ratuszowa 11, 03-450 Warsaw, Poland

^d NanoBioMedical Centre, Adam Mickiewicz University, ul. Umultowska 85, 61614 Poznań, Poland

^e Department of Macromolecular Physics, Adam Mickiewicz University, ul. Umultowska 85, 61614 Poznań, Poland

ARTICLE INFO

Keywords:

Nitrides
Carbides
Heterostructures
Thin films
Molecular dynamics simulations
Composite materials

ABSTRACT

Nanoscale multilayered TiN/SiC films are of great importance in many electronic and industrial fields. The careful control over the structure of the laminates, nanocrystalline or amorphous, is crucial for their further applicability and study. However, several limitations in their fabrication have revealed important gaps in the understanding of this system. Here, we study influence of temperature on the physico-chemical and functional properties of TiN/SiC multilayers. We will show the clear increment on hardness of the samples, while the nanocomposite structure of the layers is maintained with no increment in crystal size. We will investigate the interstitial effects and rearrangements, between the TiN/SiC phases and their role in the enhanced mechanical response. Our experiments will clearly show a change in the modulation period of the samples, pointing to interfacial reactions, diffusion of ions or crystallization of new phases. Full Investigations of the film properties were carried out using several methods of analysis: XRD, XPS, FTIR, HR-TEM and SIMS. Additionally, results were combined with First Principles MD computations of TiN/SiC heterostructures.

1. Introduction

Nitrides occupy a privilege place in the both the industry and the academy, because of their unique and versatile properties [1–4]. Nevertheless, in fields that demand high mechanical, thermal and electrical resilience, the physical, mechanical, and tribological properties of conventional ceramic hard and wear-resistant protective coatings, such as titanium nitride (TiN), are not sufficient to prevent catastrophic failure in extreme mechanical-loading conditions due to material brittleness (i.e. crack formation and propagation upon loading single-crystal B1-TiN(001) (Fm $\bar{3}$ m-225) and VN(001) layers [5]). A common strategy to address the problem of inherent brittleness in ceramics, consists in enhancing hardness/toughness by alloy or multi-layer design [6–9] or via control of the electronic structure [10–13]. This, however, does not guarantee that the protective properties are maintained at high temperatures, since the hardness and stiffness of a single-phase compound or solid solution typically decrease

monotonically with increasing temperature [14]. Hot hardness needs to be combined with improved toughness, which is generally achieved by controlling solid solution thermal stability, however, this leads to spinodal decomposition at high temperatures [15–19]. Nevertheless, the hardness achieved in the works listed above typically does not exceed ~35 GPa. The necessity of improving material protective performances continuously motivates research toward development of new superhard ($H > 40$ GPa) materials with enhanced wear and corrosion resistance combined with resistance to thermally-induced stresses [20–23]. On the other hand, nanocomposite coatings have shown improved toughness and fracture resistance, that although have provided a broad range of applications to materials, remain below the superhard values [24–30]. Nevertheless, H.W. Hugosson et al. [31] have theoretically shown that by promoting stacking-fault or multiphase interfaces, the hardness of the protective coatings can be enhanced, mainly due to the stabilization of interfacial phases and the major role that coherent interfaces can play in the stabilization of low-energy interfaces and nanodomains

* Corresponding author.

** Corresponding author.

E-mail addresses: alexp@i.ua (A.D. Pogrebnyak), coyeme@amu.edu.pl (E. Coy).

[32], these facts show the relevance of interfacial/granular electronic structure in high performance protective coatings [33,34].

Silicon carbide (SiC) and different composite materials based on it are currently among the most promising materials for industrial applications [35–37]. Due to their unique combination of physico-chemical properties, such as chemical stability, refractoriness, wear and radiation resistance, SiC-based protective coatings are widely demanded in machine-building, nuclear energy, metallurgical, chemical, gas, petroleum and petrochemical industries. Intensive studies devoted to the development of composite materials based on non-oxide compounds, such as carbon, silicon carbide or nitride, in combination with carbides or nitrides of refractory metals, are carried out actively at present [38,39]. Such compounds can be used as matrices or as reinforcing filler in the form of fibres or plates [40,41]. These composite materials are characterized by low specific mass, durability and wear resistance, and demonstrate the possibility of forming complex shapes with sharp details. Due to their high strength and heat resistance, they can be used in the aeronautics and space industries as high-temperature construction materials for gas turbines, petrol engines, heat exchangers production, etc. SiC is widely used in modern electronics as semiconducting material in superfast high-voltage Schottky diodes, MOSFET transistors and high-temperature transistors. Higher electric strength, larger band gap, higher permissible operating temperature, thermal conductivity and resistance to irradiation are among the main advantages of SiC in comparison with traditional materials, such as Silicon, Gallium arsenide, etc [42]. It is also worth mentioning that the combination of excellent electronic and mechanical properties offers many opportunities to use SiC as a material for a wide range of devices and sensors subjected to high temperatures or corrosive media, for example, regulators of electricity distribution, combustion process controllers, and uncooled radiation detectors for the new generation of aerospace materials.

Superhard heterostructures based on transition metal compounds have been thoroughly investigated during the last decade due to their exceptional applicability in electronics [43–46] and protective coatings [47]. Among them, TiN/SiN_x, ZrN/SiN_x and TiN/AlN heterostructures (nanoscale multilayers) are among the most studied systems [48–55]. It has been shown that a thin interfacial layer of B1 (rocksalt structure) SiN_x and B1-AlN can be formed between TiN layers [54]. TiN/SiC heterostructures have been studied to a lesser extent. To our knowledge, only three previous investigations have been devoted to the experimental and theoretical studies of the structural and mechanical properties of TiN/SiC nanolayered systems [56–58]. The authors [56,57] deposited nanoscale multilayer TiN/SiC films by r.f. magnetron sputtering at room temperature. They showed that the epitaxial B1-SiC (Fm3m-225) interfacial layers were formed between TiN slabs when the thickness of the SiC layers was less than 0.6–0.8 nm [56]. However, in subsequent investigations [57] the same authors revised the conclusions of their previous work [56], stating that the interfacial layer had the B3-SiC (F43m-216) Zinc blende structure. According to these reports [56,57] the crystallization of SiC (for the exact thickness of 0.6 nm, not less or greater) and the epitaxial growth between TiN and SiC layers are responsible for high hardness, which reached the value of 60 GPa. At the same time, in Ref. [57] authors presented the dependencies of hardness HV (GPa) on thickness of the TiN layers, which changed from 2.5 to 19.8 nm, while thickness of SiC remained fixed to 0.6 nm. Hardness of the coatings remained around 40 GPa for various thicknesses of the TiN layers (from 9.5 to 19.8 nm), while nanohardness reaches the values around 18 GPa. The dependencies of the universal hardness (HU) on the indenter penetration depth are provided, when the thickness of SiC changes from 0.4 to 2.4 nm, while the thickness of TiN layers remains fixed [56,57]. The theoretical study of the TiN (001)/monolayer B1-SiC heterostructure showed that it was thermally stable up to 600 K [58], whereas the interface in the TiN(111)/monolayer B1-SiC heterostructure transformed to the B3-SiC structure even at low temperatures [58]. Nevertheless, possibility of recrystallizing

thicker SiC layers has not yet been addressed. This issue remains as one of the most restrictive parameters for further implementation of SiC heterostructures in electronics and protective coatings [59–61].

Taking into account the remarkable experimental results achieved for the TiN/SiC nanolayered films deposited at room temperature [56,57], we deposited TiN/SiC nanoscale multilayers to establish the role of substrate temperature in the structural and mechanical properties of the films. In our study we have increased the thickness of SiC to ≈ 5 nm, in order to provide a fresh perspective on the crystallization dynamics of thicker layers. The aim of the present study is to investigate the influence of substrate temperature during deposition on the structure and properties of the fabricated TiN/SiC coatings via detailed experimental analyses based on XRD, XPS, FTIR, STEM, HRTEM and SIMS, which provide complementary information. Correspondingly, atomic-scale understanding of phenomena responsible for the improved properties is achieved via ab initio molecular dynamics (MD) simulations [62]. Here, we show that thicker layers of SiC are not amorphous, but show a nanocomposite structure, with small crystals embedded in amorphous phase, and that by a rather low temperature process, it is possible to improve the physico-chemical interactions between SiC and TiN layers, leading to an improved mechanical response of the samples, comparable to the response observed in super hard composites. Our results provide several novel insights for clarifying key mechanisms governing the formation and mechanical properties of modern multilayered nanoscale protective coatings.

2. Experimental and computational details

2.1. Preparation of the coatings

TiN/SiC nanoscale multilayered films were deposited by consecutive DC magnetron sputtering steps from TiN and SiC targets (72 mm diameter and 4 mm thick disks with purity of 99.9%) at different substrate temperatures, T_s = 25, 100, 200 and 350 °C (samples S-25, S-100, S-200 and S-350, respectively). In addition, single-layer TiN and SiC 700 nm films were deposited at T_s = 350 °C. The distance between the targets and the substrate holder was kept constant at 8 cm. The substrates were polished Si (100) wafers. Before the deposition, the silicon wafers were cleaned in a bath with a 5% HF solution to remove the native oxide. Afterwards, the substrates were rinsed in de-ionized water and dried in nitrogen. Finally, they were sputter-etched in argon plasma in the reaction chamber prior to deposition. The substrate bias was –50 V. The argon flow rate and working pressure were 60 sccm and 0.2 Pa, respectively. The DC power density (discharge power) values at the TiN and SiC targets were 1.72 W/cm² and 0.86 W/cm², respectively. In the case of the nanoscale multilayered films, the TiN and SiC layers were deposited for 2 min and 1 min, respectively. The total number of layers was 116. The working pressure was 10^{–3} Pa.

2.2. Experimental analyses and procedures

X-ray diffraction (XRD) investigations of the films were performed with a diffractometer “PANanalytical” using Cu K_α radiation. Low angle XRD (LAXRD) was used to analyse the layer structure of the multilayer films (Ultima IV “Rigaku”, Cu K_α radiation). X-ray reflectometry (XRR) measurements were performed on the X’pert³ MRD (XL) from PANalytical with a Cu K_α radiation source (wavelength of 1.54 Å) operating at 45 kV and 40 mA. The chemical bonding was studied by Fourier transform infrared spectroscopy (FTIR) (with a “FSM 1202” LLC “Infraspek” spectrometer). The chemical states were studied by an EC 2401 X-ray photoelectron spectroscopy (XPS) system using Mg K_α X-ray radiation (E = 1253.6 eV). The Au 4f_{7/2} and Cu 2p_{3/2} peaks with binding energies of 84.0 ± 0.1 eV and 932.66 ± 0.05 eV, respectively, were used as a reference. The pass energy was 50 eV and resolution of 0.1 eV. The films were etched for 5 min with 1.8 keV Ar⁺ ions to remove surface contaminations. The structural properties of the

Download English Version:

<https://daneshyari.com/en/article/7212132>

Download Persian Version:

<https://daneshyari.com/article/7212132>

[Daneshyari.com](https://daneshyari.com)