Wednesday Morning, May 22, 2024

Plasma and Vapor Deposition Processes
Room Palm 3-4 - Session PP3-WeM

CVD Coating Technologies

Moderators: Hiroki Kondo, Kyushu University, Japan, **Frederic Mercier**, University of Grenoble Alpes, France

8:00am **PP3-WeM-1 Area-Selective Deposition of DLC Using Optoelectronic-Controlled Plasma CVD Method***, Susumu Takabayashi (stak@ariake-nct.ac.jp),* National Institue of Technology, Ariake College, Japan **INVITED**

Diamond-like carbon (DLC) is an amorphous carbonaceous material composed of sp^2 carbon, sp^3 carbon and hydrogen. We propose a controlled DLC film synthesis by photoemission-assisted plasma-enhanced chemical vapor deposition (PA-PECVD). PA-PECVD is a DC discharge plasma with the aid of photoelectrons from the substrate on which a deep UV light irradiates. The current flows only in the UV-irradiated area and the starting voltage of the glow discharge, called photoemission-asssietd glow discharge (PAGD), becomes stable owing to plenty of photoelectrons as initial electrons. The discharge before starting PAGD occurs is photoemission-assisted Townsend discharge (PATD). The current in PATD is around 10,000 time larger than that in conventional Townsend discharge. The substrate is not subject to the sheath electric field, so minute and precise synthesis with a rate of nm/min. is realized in PATD. With PATD, we actually succeeded to fabricate a graphene field effect transistor (GFET) with a DLC top-gate dielectric and synthesize oxygen and nitrogen-doped DLC films on the order of nm thickness. With PA-PECVD, we are developing and exploring application of DLC in nano-electronics and science.

9:00am **PP3-WeM-4 Microstructure and Mechanical Properties of TiZrN and TiZrCN Coatings Grown by Chemical Vapor Deposition***, Akihiro Murakami (amurakam@mmc.co.jp), M. Okude,* Mitsubishi Materials Corporation, Japan

Chemical Vapor Deposition (CVD) method has been used for the industrial production of wear resistant coatings on cutting tools and TiCN coatingshave been widely used for several decades because of its excellent hardness, good thermal and chemical stability. New CVD coatings that is superior to TiCN are continuously explored, and it is reported that ZrN and ZrCN has advantageous properties as wear resistant coatings. However, there are few reports on TiZrN and TiZrCN coatings.

In this work, TiZrN coatings were deposited from $TiCl_4$-$ZrCl_4$-N_2-H_2 precursors at 1050°C (HT-TiZrN). And TiZrCN coatings were produced from two precursor systems: TiCl--$_4$-$ZrCl_4$-N_2-CH_4-H_2 precursors at 1050°C (HT-TiZrCN) and $TiCl_4$-$ZrCl_4$-CH_3CN-N_2-H_2 precursors at 900°C (MT-TiZrCN). All coatings were deposited on TiCN coated cemented carbide.

We investigated microstructure, crystal orientation and hardness. HT-TiZrN has granular structure and lower hardness than conventional TiCN. HT-TiZrCN has columnar-like-structure, and its hardness is close to conventional TiCN. On the other hand, MT-TiZrCN has columnar structure, (211) crystal orientation and higher hardness than TiCN. In addition, Electron Back Scattered Diffraction (EBSD) analysis revealed partial epitaxial growth of TiZrCN on TiCN.

These coatings were evaluated by turning tests of alloy steel (AISI:4140). As a result, cutting performance of MT-TiZrCN coatings was superior to conventional TiCN. It seems that higher hardness of MT-TiZrCN enhances the cutting performance.

11:00am **PP3-WeM-10 New Perspectives of Atmospheric Pressure Dielectric Barrier Discharges for the Deposition of Thin Films : From Uncontrolled Amorphous Plasma-Polymer Layers to Chemically Patterned and Crystalline (in)Organic Coatings***, François Reniers (freniers@ulb.ac.be),* Université libre de Bruxelles, Belgium **INVITED**

For more than a century, atmospheric pressure dielectric barrier discharges (DBDs) have been used industrially for gas conversion, the Siemens ozone process dates from 1857 [1], and for surface treatment. Deposition of coatings remained confidential, due to the poor control of the quality of the films. Indeed, the very small mean free path at atmospheric pressure leads to species with very low energies, and random processes due to moving filaments often occur.

We show that, nowadays, starting with organic precursors, DBD can lead to chemically well controlled and tunable thin films, with a variety of properties (hydrophobic/hydrophilic). We establish correlations between the gas phase chemistry (analyzed by mass spectrometry) and the coating chemistry (characterized by XPS and IR spectrometry)[2]. The effect of the nature of the carrier gas (Ar or He) on the roughness and chemistry of the deposited coating is evidenced and explained[3]. With the improvement of the understanding of the plasma chemistry, amorphous inorganic coatings (SiOx, TiO_2) can now be easily deposited. By controlling the substrate temperature and the plasma parameters, pure and dense crystalline TiO_2 can now be deposited by APDBDs [4]. By modifying the gas composition, introducing ammonia into the plasma, N-doped TiO2, photocatalytic (and antiviral) under visible light can now be synthesized in one single step [[].

Very recently, one could immobilize streamers in a DBD and use them to deposit, in one simple step, locally chemically patterned organic films. The local chemistry (analyzed by µXPS) is depending on the gap between the electrodes, the power impulsion mode (continuous vs pulsed), the precursor flow. A physico-chemical interpretation is proposed [6,7].

Finally, injecting a precursor for inorganic coating in such discharges with immobilized filaments, in appropriate substrate and plasma streamer conditions, crystalline spots, with multi-micron length crystal needles were for the first time synthesized.

References:

1. U. Kogelschatz, Plasma Chem. Plasma Process, 23 (2003), 1-46

2. J. Mertens et al, Thin Solid Films 671 (2019), 64-76

3. J. Hubert et al, Plasma Processes and Polymers 12 (2015), 1174-1185

4. A. Remy et al, Thin Solid Films 688 (2019), 137437

5. A. Chauvin et al, Surface and Coatings Technology 472 (2023), 129936

6. A. Demaude et al, Advanced Science 9 (2022), 2200237

7. A. Demaude et al, Plasma Chem. Plasma Process, (2023) https://doi.org/10.1007/s11090-023-10355-6

11:40am **PP3-WeM-12 Novel Metal Boride Coatings in the System Zr-Hf-Ti-B by LPCVD***, Mandy Höhn (mandy.hoehn@ikts.fraunhofer.de), M. Krug, S. Höhn, B. Matthey,* Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Germany

The synthesis of metal diboride thin films is recently attracting large interest. Boron forms binary compounds with most metals. These materials in general are high-melting, extremely hard solids with high degrees of thermal stability and chemical inertness.

In this work the preparation of mixed metal boride coatings with Me = Zr, Hf, Ti by chemical vapor deposition (CVD) is described. A low-pressure CVD (LPCVD) process using the metal tetrachlorides $MeCl_4$ (Me = Zr, Hf or/and Ti) as precursors as well as BCl_3, H_2 and Ar is applied. At a deposition temperature of 850°C and a deposition pressure of 6 kPa boride layers were prepared. The coatings were characterized with respect to phase composition, crystal structure, hardness and wear behaviour.

Layers were deposited in the binary systems $HfTiB_2$, $ZrTiB_2$ and $HfZrB_2$ as well as in the ternary system $HfZrTiB_2$. The deposited diboride layers show crystalline structures with a high hardness of up to 38 GPa. Depending on the precursor ratio layers with single phase diboride composition or a mixture of different metal diborides were obtained. Phase composition and structure were examined using SEM, EDX and EBSD-analysis. The measured tensile stress in the obtained coatings depends on the deposition conditions and varies between 300 MPa and 800 MPa.

A strong adherence on hardmetal inserts is achieved by using a thin TiN bonding layer prior the diboride deposition. Scratch test measurements showed critical loads of about 90 N. In cutting tests a high performance of the CVD diboride coatings was observed. $HfZrTiB_2$ coated inserts showed a higher lifetime in comparison with state-of-the-art CVD-TiB_2 coatings in face-milling of TiAl6V4.

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