Project title: Novel metastable thin film materials through potential energy dissipation during subplantation of multiply charged ions (Microcon)

Project number: K128/2018

Executive Summary

The project started in May 2019 involving two strong groups in the field of plasma-based thin film deposition technologies: the Plasma Engineering Group of the Leibniz Institute of Surface Engineering (IOM) and the Materials Chemistry Chair of RWTH Aachen University. The scientific focus of the project is to control and change the ion charge state to explore the effects of potential and kinetic energy of ions on thin film properties using mostly cathodic arc deposition. The structural and functional properties of the films are investigated for relevant applications. An additional focus of the project is to increase the scientific and societal relevance of the groups by building a strong collaborative network between the groups and by transferring the experience of the project leaders to the younger scientists involved.

The project had the motivation to build an excellent, multinational research team. After hiring qualified researchers (from Germany, Iran and Turkey), IOM has focused on thin film deposition, building a custom designed filtered cathodic arc system and on high resolution materials characterization. Following the objectives of the project, the arc deposition system has been installed in a vacuum chamber, including a macroparticle filter and a set of plasma diagnostic tools. Detailed plasma investigations for different electrical configurations and high quality reproducible thin film depositions were performed at IOM. At RWTH, the Materials Chemistry group has focused on density functional theory based molecular dynamic simulations for VAlN films to mimic the plasma-surface interactions and depositions of films with HiPIMS and cathodic arc deposition. Both institutions have achieved the milestones of the project as proposed with slight modifications.

VAlN thin films have been deposited at RWTH by HiPIMS, and at IOM by filtered cathodic arc deposition and extensive material characterization has been performed for the films and deposited films exchanged for different type of materials characterization. Advanced characterization techniques are used such as transmission electron microscopy (at IOM) and atom probe tomography (at RWTH). Chemical compositions of thin films were measured at the Ion Beam Center with elastic recoil detection analysis (ERDA) at the Helmholtz Zentrum in Rossendorf. An experimental approach has been developed at IOM for the first steps of decoupling the effects of the ion kinetic and potential energies on forming thin film microstructure. The contributions of high flux of multiply charged ions to form crystalline thin metastable VAlN cubic films at room temperature has been demonstrated. RWTH focused on ab-initio calculations to mimic plasma-surface interactions and comparing the effects of different deposition methods such as HiPIMS and cathodic arc deposition regarding the film microstructure and functionalities of VAlN or TiAlN films. The results of the project are presented at national and international conferences, summarized in one Master and two PhD theses. The main results of this project are summarized in three open access publications in peer reviewed journals and six other articles are published as a results of collaborations.

The project progress and other research activities were presented/discussed in regular meetings and workshops between the two groups. Both institutions supported the further development of the employees during the project. The researchers hired by the project gained new scientific and professional skills, while the PhD student at RWTH obtained a position in a leading international company; the postdoc is given new responsibilities as a group leader at IOM.

Due to parental leave of the employee at IOM, the project was on temporary hold from August 2020 to April 2021. Additionally, the project was extended for 3 months at no additional cost.

1. Achievement of objectives and milestones

Milestone 1 (Year 1) at IOM: The custom design cathodic filtered arc deposition system (comprised of an arc plasma source, magnetic coil, macroparticle filter, power suppliers, substrate holder) was installed in a vacuum chamber together with the plasma diagnostic tools. The proper operation of the cathodic arc deposition system was demonstrated, plasma properties of the V-Al system have been measured and initial VAlN films were grown. The enhancement of the charge states of film-forming ions was achieved by using a magnetic coil in the arc source and measured by an energy-selective mass spectrometer. The work packages (WPs) in year 1 were almost fulfilled except the regular film deposition, which was caused by the delays in the vacuum chamber delivery to IOM by the supplier due to unforeseen issues with the technical controls. The postdoc at IOM focused on transmission electron microscopy (TEM) training, selected area electron diffraction (SAED), and X-ray reflectivity (XRR) analyses for characterization of the films. The (V,Al)N thin films deposited by the project partners in RWTH have been characterized at IOM by TEM, SAED, and XRR techniques.

Milestone 1 (Year 1) at RWTH: The computational materials science training was completed by the PhD student and density functional theory based molecular dynamic (DFT-MD) simulations for VAlN was performed to theoretically mimic the plasma-surface interactions. Since the thin film growth activities at IOM were delayed (see explanations above), VAlN thin films were first deposited at RWTH using high-power impulse magnetron sputtering (HiPIMS) technology. This research strategy enabled us to probe similarities and differences between arc and HiPIMS plasma regarding their influence on phase formation, microstructure evolution, and consequently mechanical properties of the as-grown coatings with similar chemical composition. Extensive materials characterization was performed, including focused ion beam (FIB) technique for electron microscopy investigations. In addition, atom probe tomography (APT) has been performed to study the local chemical composition of VAlN films.

Milestone 2 (Year 2) at IOM: As proposed, plasma characterization for different electrical configurations were investigated by using energy-selective mass spectrometry and the effects on the deposited thin films. The most important parameters to control the ion charge state was found to be applying an external magnetic field at the plasma source. With respect to maximizing the ion charge state, magnetic field together with the optimum gas pressure are identified, 0.2 T and 0.2 Pa, respectively. The process was reproducible, deposited films were macroparticle free, dense and crystalline. Detailed materials characterization was performed with XRD, SEM, XRR, TEM and SAED for IOM and RWTH samples. The effect of cathode chemical composition on forming stable wurtzite phase or desired metastable cubic phase of VAlN films were studied. The first indications on the effect of *"atomic scale heating"* versus *"substrate heating"* has been observed regarding thin film crystallinity.

Milestone 2 (Year 2) at RWTH: The ion energy range studied in year 1 was extended both theoretically and experimentally to cover energies up to 200 eV. Again, extensive materials characterization with integral and spatially resolved structural and chemical probes was performed on VAlN films. High resolution structural characterization on films grown at RWTH was performed at IOM. This led to a joint publication in Acta Materialia (Vol 214, p117003, 2021) references are listed in the attached Excel file.

Milestone 3 (Year 3) at IOM: The focus of the final year was shifted (instead of extending the materials system) to the clear separation of (i) *"atomic scale heating"* versus *"substrate heating"* and (ii) *kinetic energy* versus *potential energy of ions* on thin films structure. The films were deposited at room temperature and at 500 °C substrate temperature. A systematic experimental approach was developed to control and enhance the ions' potential energy towards distinguishing the contributions stemming from kinetic and potential energies of ions on the film growth. However, further research is needed to assess and distinguish the additional effect of ion flux on thin film structure. The results are summarized in a manuscript and published in JVST A (*Vol* 41, 063106, 2023).

Milestone 3 (Year 3) at RWTH: The research strategy developed in years 1 and 2 was employed to study TiAlN in an ion energy range of up to 200 eV. Again, extensive materials characterization with integral and spatially resolved structural and chemical probes was carried out, as performed on VAlN films. High resolution structural characterization on films grown at RWTH was performed at IOM. This led to another joint publication in Acta Materialia (Vol 250, p118864, 2023); references are listed in the attached Excel file.

2. Activities and obstacles

Year 1 at IOM: The custom-designed filtered cathodic arc system was installed with a delay beyond our control. In the meantime, the technical staff focused on the design and the implementation of the cathodic filtered arc system, and the postdoc focused on the materials characterization and became a regular user of TEM to characterize the samples from deposited at RWTH and IOM. The initial plasma process was characterized by an energy-selective mass spectrometer, which allowed us to measure ion energy distribution function for different ions and their charge states. By using the electromagnetic coil in the discharge region, a shift of the ion charge states was shown, and VAlN films were deposited.

Year 2 at IOM: Well-characterized regular thin film deposition of VAlN films was achieved by optimization and characterization of plasma flow. The most important plasma process parameters are identified to control the potential energy of ions and possibly distinguish between the effects stemming from the kinetic versus potential energies of ions on thin film properties. Optimum process parameters were defined for reproducible, macroparticle-free film deposition. VAlN films deposited at RWTH by HiPIMS were characterized at IOM by XRD, XRR, and TEM/SAED. A collaboration with Ion Beam Center in Helmholtz-Zentrum Dresden-Rosendorf was established for compositional measurements of selected thin films by ERDA.

Year 3 at IOM: A systematic experimental approach was developed consists of operating (i) simple arc source as a reference, (ii) plasma biasing to increase kinetic energy and (iii) applying external magnetic field to enhance ion charge state to reveal the effect of potential energy of ions as compared to kinetic energy of ions on the growing films. Detailed structural characterization was carried out together with chemical composition analysis. Using the external magnetic field at the plasma source was identified as the most effective "knob" to control and enhance the potential energy of ions. The *"atomic scale heating"* effect was demonstrated as compared to substrate temperature regarding the crystallinity of thin films, which can be crucial for coatings on temperature-sensitive substrates. However, using an external magnetic field leads to an increase of the ion flux and the decoupling of the different energy contributions is not completely decoupled. Results are summarized in a joint manuscript, published in JVST A (*Vol* 41, 063106, 2023). Growth of extended material systems is not performed since the fundamental findings of the project were complex and required deeper studies than initially planned. However, Al films deposited for the PhD thesis of K. Oh, indicating that using multiply charged ions changes the microstructure of metallic films as well. Thus, the approach developed in this project can be extended to different materials systems.

Year 1 at RWTH: Synthesis of VAlN thin films was addressed at RWTH by using HiPIMS in an industrial scale deposition system. Firstly, HiPIMS discharges in Ar and N_2 atmosphere were characterized by energy-resolved mass spectrometry. The ion energy distribution functions were recorded and used as input parameters in a correlative experimental and theoretical model. Here, the influence of the kinetic energy of ionized species on the structure evolution and, consequently, on the mechanical properties of VAlN thin films has been systematically investigated. The computational materials science studies of VAlN were performed by using a DFT-MD approach to mimic the ion irradiation effects on the growing film surface on an atomistic scale. The model provides the defect structure evolution as a function of the kinetic energy of ions in the range of experimentally relevant energies. The final chemical composition, defect structure, mass density, stress state and consequently the elastic modulus of VAlN were then obtained theoretically with respect to the initial ion kinetic energy.

Year 2 at RWTH: The correlative experimental and theoretical study of the influence of ion kinetic energy on the final defect structure and mechanical properties of VAlN thin films was summarized in a joint publication between RWTH and IOM published in Acta Materialia in 2021: Specifically, we systematically studied the ion irradiation-induced changes in the structure and mechanical properties of metastable cubic (V,Al)N deposited by reactive high power pulsed magnetron sputtering by correlating experiments and theory in the ion kinetic energy (E_k) range from 4 to 154 eV. Increasing E_k resulted in film densification and the evolution from a columnar (111) oriented structure at $E_k \leq 24$ eV to a fine-grained structure with (100) preferred orientation for $E_k \geq 104$ eV. Furthermore, the compressive intrinsic stress increased by 336 % to -4.8 GPa as E_k was increased from 4 to 104 eV. These ion irradiation-induced changes in the thin film stress state are in good agreement with density functional theory simulations. Furthermore, the measured elastic moduli of (V,Al)N thin films exhibit no significant dependence on E_k.

Year 3 at RWTH: The developed research strategy in the first 2 years was applied to TiAlN system and summarized in a joint publication between RWTH and IOM published in Acta Materialia in 2023: Here, ion-irradiation-induced changes in structure, elastic properties, and thermal stability of metastable c-(Ti,Al)N thin films synthesized by high-power pulsed magnetron sputtering (HPPMS) and cathodic arc deposition (CAD) were systematically investigated by experiments and density functional theory (DFT) simulations. While films deposited by HPPMS showed a random orientation at ion kinetic energies E_k>105 eV, an evolution towards (111) orientation was observed in CAD films for E_k>144 eV. The measured ion energy flux at the growing film surface was 3.3 times larger for CAD compared to HPPMS. Hence, it is inferred that the formation of a strong (111) texture in CAD films is caused by the ion flux- and ion energy-induced strain energy minimization in defective c-(Ti,Al)N.

3. Results and successes

Regular meetings and workshops were organized with an extended list of participants from both sides. In total 5 workshops were organized during the project, each of them effectively lasted 1 full day, and numerous online meetings were organized to discuss the project. Due to the Covid pandemic, most of the meetings were online. Two in-person workshops were organized, the first one at RWTH and the last one at IOM, including lab tours. The project is successfully completed in a well-developed collaboration between the partners; the direct project results were presented in conferences, three articles as main outcome were published as open access. Moreover, the project results from both institutions cover a portion of PhD theses of S. Karimi Aghda and K. Oh. Master thesis by H. H. Sua contributed to the design of VAlN and VAlON thin films. The funded project allowed us to leverage collaborations which led to the additional six publications. All publications and theses are listed in the attached Excel file. Additionally, the project results presented in EMRS Spring Meeting (2023&2022), Plasma Surface Engineering (2022) and 20th Plasma Technology Conference (2022- invited talk).

4. Equal opportunities, career development and internationalization

At IOM, issues of equal opportunities, non-discriminatory cooperation, and work-life balance are important parts of the work culture. The equal opportunity officers strictly follow the conditions at the institute and an equality plan is completed every 4 years. Additionally, the "cascade" model is implemented to further promote equal opportunities and increase the percentage of women. The IOM also strives to increase the number of international staff. At RWTH, promotion of equality is organized through the Equal Opportunities Officer and her deputy representatives. They are involved in the University's council and committee work, regularly participate in meetings of the Rectorate, the Board of Governors, Senate, and Equal Opportunities Committee, contribute to the creation of the Equal Opportunities Plan, and are involved in hiring and appointment processes (IGaD – 2017-2022).

Specific to this project, a female Turkish postdoc (at IOM), a male Iranian PhD student (at RWTH) were hired, and a Korean male PhD student was partially employed. The students received their degree from RWTH Aachen University and University of Leipzig, respectively. While the graduated students found positions in leading international industrial organizations, the postdoc received a group leader position and was appointed a diversity officer at IOM.

5. Structures and collaboration

The research team at IOM
Project leader: Prof. Dr. André Anders
Postdoc: Dr. Yeliz Unutulmazsoy (07/2019 – 6/2022 – inc. parental leave)
Technical Staff: Jens Knipper (06/2019 – 02/2023 – inc. parental leave),
PhD Student: Oh Kyunghwan, M.Sc. (01/2022-03/2022)

The research team at RWTH Aachen
Project leader: Prof. Dr. Jochen Schneider
PhD Student: Philipp Keuter, M.Sc. (05-12/2019), Soheil Karimi Aghda, M.Sc. (08-09/2020)
Postdoc: Dr. Dimitri Bogdanovski (since 07/2019-12/2021), Dr. Stanislav Mráz (08-09/2020), Dr. Lukas Löfler (02-12/2022), HiWi: Heng Han Sua, B.Sc. (06-12/2020)

6. Quality assurance

There were no experiments on animals in this project. At IOM and RWTH, the following guidelines are binding for all scientific work:

1- Guidelines on Safeguarding Good Scientific Practice and on Dealing with Allegations of Scientific Misconduct within the Leibniz Association (specific to IOM),
2- Principles for safeguarding good scientific practice at RWTH Aachen University and guidance is provided by education offered by the Center for Professional Leadership (specific to RWTH)
3- Guidelines on safeguarding good scientific practice, “Kodex” and Rules of Procedure for Dealing with Scientific Misconduct of DFG.

7. Additional resources

IOM supplied the vacuum system valued at approx. 300 T€ for this project. Furthermore, IOM supports the setup and maintenance cost of characterization equipments, and in particular of the microscopy “Titan”, at an annual cost of approx. 100 T€, which was crucial for the project. A strong team was created to achieve success in this project, a technician and another postdoc at IOM supported the project. RWTH provided a computing infrastructure for *ab initio* calculations of approx. 50 T€. The maintenance of equipments, i.e. FIB and APT, was supported with an estimated contribution of 10T€ each. Moreover, the investment of additional personnel contributed to the project at RWTH. The employees were encouraged to attend conferences, also by using the in-house budget to present the achievements of the project.

8. Outlook

The current project revealed the effect of multiply charged ions in cathodic arc deposition with an in-house designed experimental set-up on thin films. The project demonstrated the possibility of depositing crystalline VAlN thin films. However, while the project could show the first steps to decouple the kinetic and potential energies of ions on thin film properties, another effect is involved is the “ion flux. Therefore, the future work on eliminating the ion flux effect is crucial to clearly distinguish the effect of ion potential energy on thin films. This project has drawn the guidelines to decouple the kinetic and potential energies of ions and demonstrated that the effect of potential energy of ions on thin film properties are not trivial. Currently a project proposal is under preparation to be submitted to DFG. Since the project could show that it is possible to grow crystalline thin films at room temperature, growing coatings with cathodic arc at given optimum conditions for temperature-sensitive substrates could be crucial for developing future technologies, for example PVD grown barrier layers on flexible, temperature-sensitive substrates.