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Publication Date
1995-04-01

LBL-37091
UC-404

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Accelerator & Fusion Research Division

Presented at the Ninth Annual Conference on Fossil Energy Materials, Oak Ridge, TN, May 16–18, 1995, and to be published in the Proceedings

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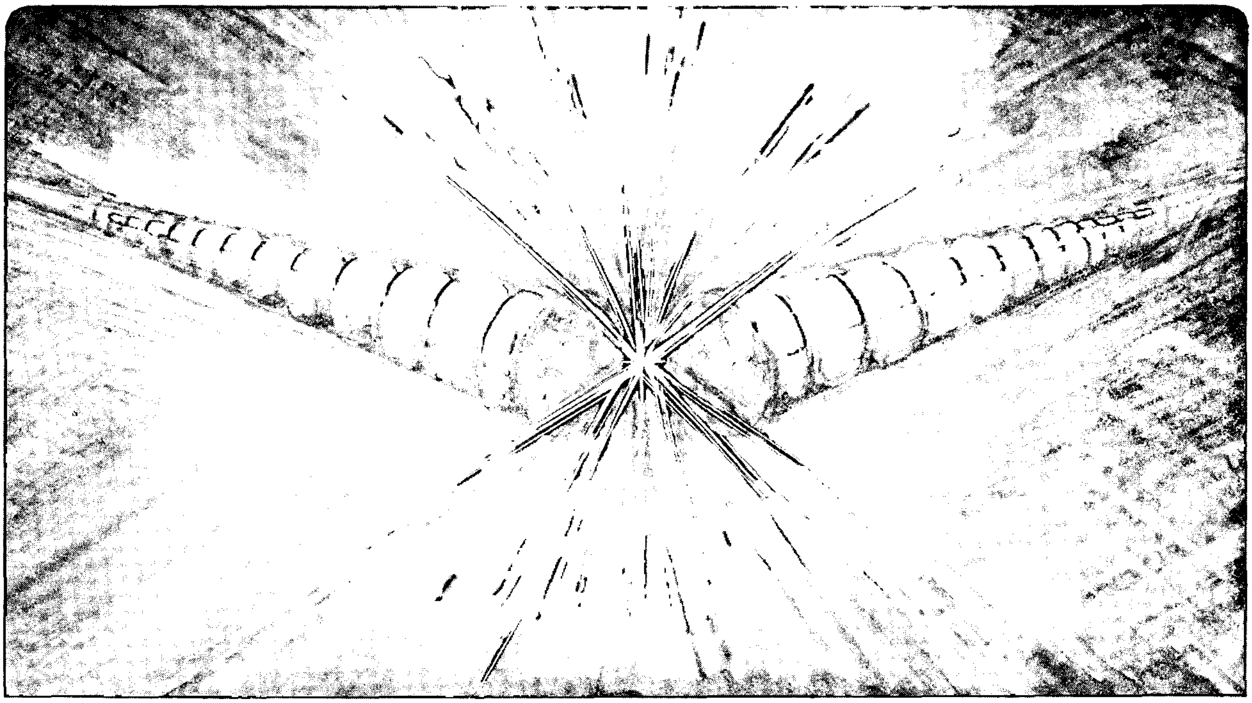

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

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PLASMA SYNTHESIS OF ALUMINA FILMS ON METAL & CERAMIC SUBSTRATES

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This work was supported by the U.S. Department of Energy, Office of Advanced Research, Fossil Energy, under Contract Number DE-AC03-76SF00098.

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ABSTRACT

We are exploring the feasibility of the plasma synthesis of highly-adherent films of alumina and chromia on SiC and FeAl substrates. A magnetically-filtered cathodic arc plasma deposition technique is used in which a high density metal plasma (Al or Cr) is formed and deposited on the substrate in the presence of a low pressure gaseous oxygen background. The substrate is simultaneously repetitively pulse biased, providing a means of controlling the incident ion energy. In the early stages of the process the ion energy is held in the keV range so as to produce atomic mixing at the film-substrate interface (ion stitching), and in the latter stages of deposition the energy is reduced to ~200 eV (IBAD range) to provide a means of controlling the film structure and morphology. Films that are dense and highly adherent can be formed in this way. We have produced near-stoichiometric films of alumina and chromia on small SiC and FeAl substrates and characterized the films in a number of ways, including RBS, X-ray diffraction and adhesion, and we've also done some preliminary temperature cycling experiments. The alumina films are of thickness from 0.2 to 1.5 μ, amorphous prior to heat treatment, and show an α-alumina phase after heat treating at 1000°C for up to 16 hours. The film substrate adhesion is typically greater then ~70 MPa prior to heating, and initial results indicate that the films maintain their adhesion after repetitive cycling in temperature between ambient and 1000°C. Here we describe the plasma processing method and outline the experimental results obtained to-date.

INTRODUCTION

Vacuum arc plasma discharges are intense sources of highly ionized, dense metal plasmas. Plasma generators based on this kind of discharge can be used to deposit thin films of various kinds including metals and alloys, and if the source is operated in a gaseous background then compounds including ceramic oxides can also be formed. We have developed techniques that combine plasma deposition with ion bombardment to create a powerful and adaptable new technology that is environmentally friendly, highly efficient, can be scaled up to large size, and can synthesize films of a range of materials[1-4]. The films can be atomically mixed to the substrate by the ion bombardment phase of the process to produce excellent film/substrate bonding at the atomic level.

A metal plasma of the required species is formed by a vacuum arc plasma gun and directed toward the substrate with a moderate streaming energy, typically of order 100 eV. At the same time, the substrate is repetitively pulse biased to a moderate negative voltage (typically a few hundred to a few tens of kilovolts), thereby accelerating a fraction of the incident ion flux and energetically bombarding the ions into the substrate and the previously-deposited film. This technique provides a means for precise control of the energy of the depositing plasma ions. We use an early-time high ion energy so as to atomically mix the film into the substrate, and a lower (but optimized) ion energy during the bulk of the film growth so as to add an 'ion assist' to the deposition (similar to an ion beam assisted deposition, or IBAD, process). In this way the film is ion stitched to the substrate and has very strong adhesion, and it is also of high density (void-free), good structure (eg, not columnar), and good morphology (eg, close to atomically smooth).

In the work described here, we've used this plasma materials synthesis technique to form films of Al_2O_3 and Cr_2O_3 on SiC and FeAl substrates. The films have been characterized, both before and after 1000°C heat treating, for composition and phase using Rutherford backscattering spectrometry (RBS) and X-ray diffraction analysis, and the film-substrate adhesion has been measured using a Sebastian-type pull tester. In the following we firstly outline the plasma and ion beam processing set-up, the substrate preparation, and the characterization methods used. The experimental results of the program to-date are then presented. Finally, we discuss the implications of the work and possible extensions of the method for this field of application.

EXPERIMENTAL PROCEDURE

Plasma Processing

We've made a number of different kinds of vacuum arc plasma guns, from small pulsed versions to a large dc embodiment. The sources can be operated either in a repetitively pulsed mode with pulse duration between 50 μs and 5 ms, or with long pulses (tens or hundreds of milliseconds), or d.c.; arc current is typically in the range 100 - 250 A. The guns are UHV-compatible and the cryogenically-pumped system base pressure is typically about 1×10^{-6} Torr. For the alumina and chromia films produced in this work, we used a "minigun" (Fig. 1) with arc pulses of 5 ms duration and at a repetition rate of about 1 pulse per second. The cathode is a central cylindrical rod of the desired metal plasma species surrounded coaxially by a cylindrical anode. The arc pulses are initiated by a short (~10 μs) high voltage (~10 kV) trigger spark to the cathode. The plasma is created on the cathode surface and leaves the source as a directed plume through the annular anode. It is a fundamental characteristic of this kind of plasma discharge[5,6] that along with the plasma formation, a small fraction of 'macroparticles' is also produced – small particles of metallic cathode debris of dimension in the range 0.1 - 10 μ. If macroparticle filtering is desired, as for the present purpose, a magnetic duct of suitable size is attached so that the plasma streams directly from the plasma gun into the filter[7]. With optimum magnetic field configuration[8,9] and optimum bias of the filter wall, about 25% of the ions produced in the arc discharge can be transported through the filter. Figure 2 shows plasma flowing through the magnetic filters used in the present work. The overall plasma deposition system thus consists of the repetitively pulsed plasma gun in conjunction with the 90° bent magnetic filter. Plasma exits the filter and deposits onto the appropriately positioned substrate.

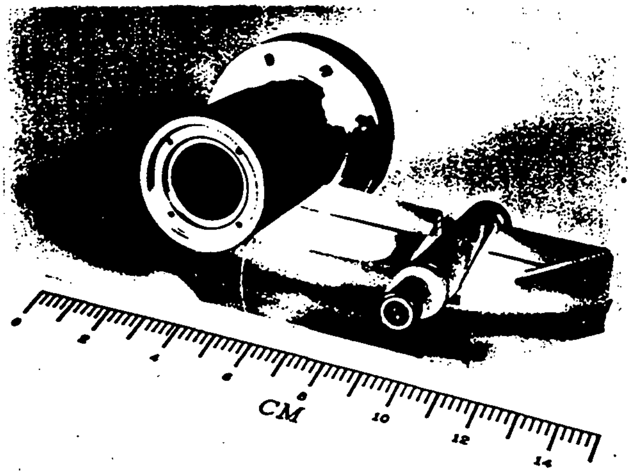

Figure 1. Partially disassembled vacuum arc plasma gun of the kind used here. The cathode assembly is shown removed from the anode.

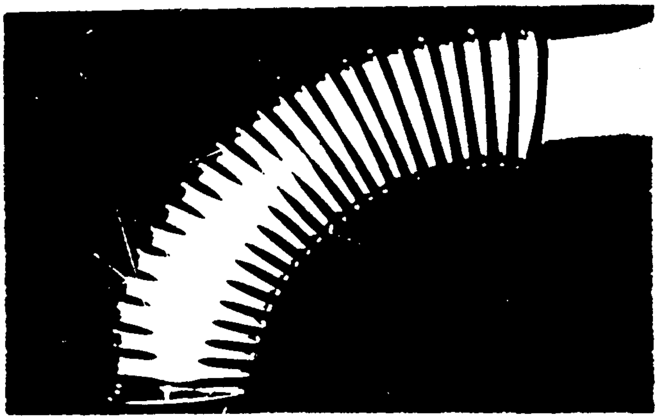

Figure 2. Magnetic filter, showing plasma injected from the gun at the lower left streaming through it and exiting at the upper right.

Films of metallic oxides can be formed simply by carrying out the plasma deposition not in a high vacuum environment, but in a somewhat higher pressure ambient of oxygen gas[10,11]. We have found empirically that a pressure in the range 1 - 100 mTorr is suitable for most metal oxides. Here the oxygen background pressure was 10 to 15 mTorr. The oxygen is both entrained in the plasma stream, ionized, and deposited in the plasma state, as well as reacting at the freshly-deposited metallic surface to form aluminum oxide. The net result is that, for the optimal oxygen pressure, a stoichiometric film of alumina is formed.

Ion energy of the depositing plasma flux is controlled by repetitively pulse biasing the substrate. Typically the pulse duration might be ~10 μs and the duty cycle ~10 - 50%. Pulsing of the bias voltage is necessary (for all but the lowest bias voltages) because a high voltage dc bias would cause an electrical discharge between the substrate and the vessel or the plasma gun; the plasma would be grossly perturbed (because the plasma sheath would expand from the substrate to large distances) and the ions would not be accelerated. The solution is to switch off the bias before such major perturbation can occur (to limit the sheath expansion to modest distances), let the plasma recover, and then to repeat the process; ie, to do the biasing in a repetitively pulsed mode. For the early stages of the deposition process the pulse bias is held at a relatively high voltage of 2.2 kV. The mean aluminum ion energy is then 3.75 keV, because the mean ion charge state of the aluminum plasma is 1.7 (ref. 12) and $E_i = QV$. This energy results in an implantation into the substrate to a depth of up to ~100 Å, causing intermixing of the early-phase Al film that is deposited during the pulse-off part of the pulse biasing. The aluminum film thus grows on the SiC substrate from a highly mixed interface. When aluminum oxide is formed, the oxygen is also intermixed both by direct implantation of ionized oxygen as well as by recoil implantation of oxygen in the surface film. When a film thickness of just a few tens of angstroms has accumulated, the pulse bias voltage is reduced, since intermixing with the substrate is no longer a factor and the higher ion energy would give rise to a high degree of sputtering of the already-deposited film. Moreover, it is known from a large body of work on ion assisted deposition that a modest ion energy can be highly advantageous in terms of providing a means for controlling such characteristics as the density, morphology and structure of the depositing film. For the bulk of the plasma deposition process the pulse amplitude is kept at 200 volts.

Substrate Preparation

The substrates were small coupons of silicon carbide and iron aluminide. The SiC was CVD-produced and was purchased from Morton Advanced Materials; the coupons were 0.5" x 0.5" square and 0.1" thick, and were polished. The FeAl was supplied by ORNL, and was in the form of polished 1 cm x 2 cm coupons approx. 1 mm thick.

Characterization

Analysis of film composition was done with Rutherford backscattering spectrometry (RBS) using 1.8 MeV He^+ ions, and X-Ray diffraction analysis was used to determine the crystallographic phase. Film adhesion was measured with a Sebastian-type pull tester using Sebastian studs epoxied to the samples and pulled normal to the substrate by known weights; the epoxy failure limit was typically ~70 MPa, and this thus determined the instrumental limit.

Procedure

Substrate samples were cleaned with alcohol and positioned within the vacuum chamber for the plasma deposition and ion bombardment processing. The oil-free system was cryogenically pumped down to a base pressure of about 1×10^{-6} Torr or better before commencing the plasma process. Oxygen gas was admitted to a pressure of typically 10 to 15 mTorr, and the plasma deposition and ion bombardment processing carried out as described above; the time required for film growth was usually a few tens of minutes. Note that in this plasma processing the energy added to the sample is small and they are not heated significantly. The samples were then removed from the chamber for characterization and testing. Heating was done in air in an oven which could be heated to 1100°C. The samples could be inserted into and removed from the hot oven quickly, and the sample heat-up and cool-down time was thus just a few minutes, determined by the thermal capacity of the small coupons. In the experiments conducted, the samples were maintained at full temperature at times varying between 15 minutes and 16 hours.

EXPERIMENTAL RESULTS

A number of different samples were prepared and studied, of both alumina and chromia and on both silicon carbide and iron aluminide. Several different thicknesses of films were formed, between about 0.2 µ and 1.5 µ. Issues that we considered important to address were:

- Stoichiometry of the plasma deposited film, both pre- and post-heat treatment;
- Crystallographic phase of the film produced, pre- and post-heat treatment;
- Adhesion of the film to the substrate, pre- and post-heat treatment;
- Adhesion of the film to the substrate following thermal cycling of the sample through a number of repeated high temperature excursions.

Stoichiometry

RBS analysis of the alumina films showed that that the as-prepared samples were usually slightly oxygen-rich, with composition such as for example $Al_2O_{3.3}$, for a background oxygen processing pressure of 12 mTorr. When the oxygen pressure was too high, for example 26 mTorr as in our early work, the films were significantly oxygen rich, showing an Al_2O_5 composition. The post-heating films were, not surprisingly, of good Al_2O_3 stoichiometry.

Crystallography

The as-deposited alumina was typically amorphous with a small amount of κ-Al_2O_3, but for optimized plasma and ion beam processing conditions and oxygen gas pressure, we could form material containing largely α- and κ-Al_2O_3 (Fig. 3). The post-heating films were always largely α-Al_2O_3 (Fig. 4).

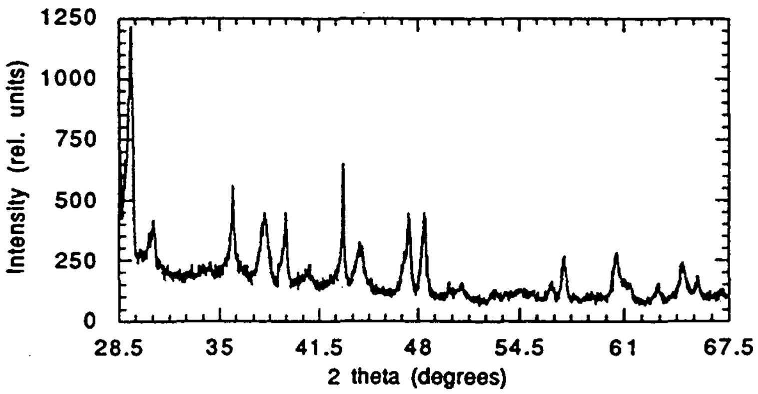

Figure 3. X-ray diffraction spectrum for an alumina film, as-deposited (pre-heating) at optimal conditions, indicating mostly α- and κ-Al_2O_3 phases. Film thickness 0.5 μ; on FeAl.

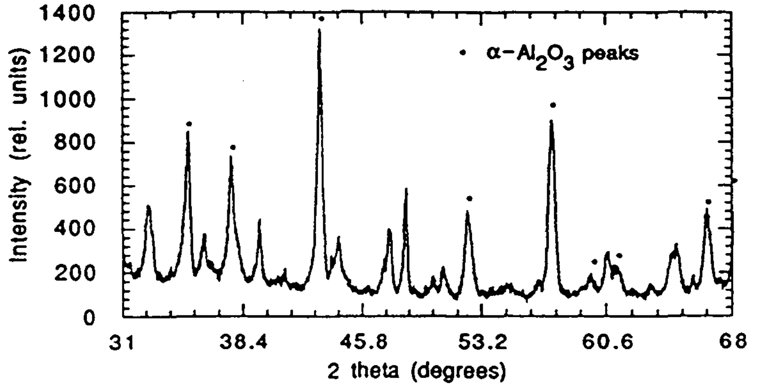

Figure 3. X-ray diffraction spectrum for an alumina film, after heating at 1000°C for 16 hours, indicating mostly α-Al_2O_3 phase. Film thickness 0.5 μ; on FeAl.

Adhesion

The film-substrate adhesion was always good for the as-prepared, pre-heat-treatment films – an adhesion strength as measured with our home-made Sebastian-type pull tester of $\gtrsim 70$ MPa, the instrumental limit of measurement – this for both alumina and chromia films on both FeAl and SiC. Post-heat-treatment, the adhesion strength of the optimally-prepared films is also good for films of thickness $\lesssim 0.5\ \mu$, but we've had mixed results to-date with films of thickness $\gtrsim 1\ \mu$. We refer here to heating to 1000°C for a period of either 15 minutes or 16 hours (we've done both), for a single heat cycling.

Adhesion after Repeated Thermal Cycling

We have at the present time data for one set of experimental conditions only. These data are for an alumina film of thickness about 0.25 μ formed on a SiC substrate. The sample was thermally cycled from room temperature to 1000°C though four cycles of 15 minutes duration each; heating and cooling time of the sample was one or two minutes only. The film-substrate adhesion both before and after temperature cycling was excellent, at the instrumental limit of the pull-tester.

CONCLUSION

Films of alumina (and also chromia) have been plasma synthesized on FeAl and SiC substrates. The process is straightforward and produces a mostly α-Al_2O_3 phase. The plasma deposition process is accompanied by a controlled and time-varied ion bombardment such that the film is atomically mixed to the substrate and consequently of high adhesion, and the ion-assist process during the bulk of the film growth helps to form good morphology. For optimally prepared films the film-substrate adhesion is $\gtrsim 70$ MPa, and at least for quarter-micron alumina films on SiC the film retains its integrity and full adhesion strength through a 4-cycle thermal cycling between ambient and 1000°C.

We have reported here on the status at the time of writing of our program to explore the feasibility of the plasma synthesis of alumina and chromia films on silicon carbide and iron aluminide substrates. Clearly there's much work that remains to be done. We can conclude, however, that the plasma and ion beam techniques described here provide a tool that could make a valuable contribution to the field.

Acknowledgements

We are indebted to Peggy Hou, Simone Anders, André Anders and Kin-Man Yu for help in various parts of the work, and to Bob MaGill and Mike Dickinson for support of the experimental equipment. This work was supported by the U.S. Department of Energy, Office of Advanced Research, Fossil Energy, under Contract Number DE-AC03-76SF00098.

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