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PLASMA AND ION BEAM SURFACE MODIFICATION AT LAWRENCE BERKELEY NATIONAL LABORATORY

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Surface processing by metal plasma and ion beams can be effected using the dense metal plasma formed in a vacuum arc discharge embodied either in a “metal plasma immersion” configuration or as a vacuum arc ion source. In the former case the substrate is immersed in the plasma and repetitively pulse-biased to accelerate the ions across the sheath and allow controlled ion energy implantation + deposition, and in the latter case a high energy metal ion beam is formed and ion implantation is done in a more-or-less conventional way. These complementary ion processing techniques provide the plasma tools for doing ion surface modification over a very wide range of ion energy, from an IBAD-like method at energies from a few tens of eV to a few keV, through ion mixing at energies in the ~1 to ~100 keV range, to 'pure' ion implantation at energies of up to several hundred keV. New hybrid processing schemes that combine the different ion energy regimes can also be explored and used in a single fabrication / modification process to make novel surfaces of complex design. Some of the applications to which we've put these plasma and ion beam tools include, for metal plasma immersion processing: doped diamond-like carbon (dlc), novel multilayers, alumina and more complex ceramic materials such as mullite ($3Al_2O_3.2SiO_2$), high temperature superconducting films, biomedical compatibility, and more; and for high energy ion implantation: metallurgical wear resistance, surface resistivity tailoring of ceramics, rare-earth doping of III-V compounds, and more. Here we review the fundamentals of the techniques, describe the plasma and ion beam hardware that has been developed, and outline some examples of the materials applications to which we’ve put the methods.

INTRODUCTION

Plasma and ion beam methods for material surface modification [1] span the energy range from a few electron volts for low energy plasma deposition methods up to hundreds of keV for high-energy ion implantation. Hybrid methods such as ion beam mixing and ion beam assisted deposition (IBAD) have also been well developed. All of these methods have the powerful advantage that the medium constituting the incident flux is composed of electrically charged species and so can be manipulated by electric and magnetic fields – in particular, the incident ion energy can be controlled – in contrast to other methods such as sputtering and evaporation where the depositing flux is neutral and cannot be readily controlled.

Vacuum arcs, also called cathodic arcs or metal vapor arcs, [2-4], provide an efficient and simple method for producing large amounts of dense metal plasma that can be used for plasma deposition of thin films [5], or incorporated into an ion beam source [6,7] for doing energetic ion implantation. In another approach, called plasma immersion ion implantation [8], the substrate itself is biased negatively, either repetitively pulsed or (in some cases) dc, while “immersed” in the plasma, thereby providing a means of controlling the energy of the depositing ion flux and allowing processing that can vary from deposition to energetic ion implantation. These complementary plasma and ion beam processing techniques provide the plasma tools for carrying out surface modification over a very wide range of particle energy, from an IBAD-like deposition at a few tens of eV to a few keV, through ion mixing at energies in the ~1 to ~100 keV range, to 'pure' ion implantation at energies of up to several hundred keV. New, hybrid processing schemes that combine the different ion energy regimes can also be used in a single fabrication / modification process to make novel surfaces of complex design.

The range of processing methods addressed here thus includes the application of vacuum arc plasmas for the formation of thin films that have been “structure-optimized” and ion stitched to the substrate by energy-controlled metal plasma immersion techniques, and ion implantation using energetic metal ion beams formed from vacuum arc plasmas. The methods have been developed and used by a growing number of researchers at laboratories around the world, and much excellent work has been done. Here we review the methods and hardware that have been developed by our group at Berkeley, and summarise some examples of the materials synthesis and modification applications that have been explored in the course of our work.

PLASMA AND ION BEAM TECHNIQUES

Vacuum Arc Produced Metal Plasma

The vacuum arc (or cathodic arc) is a high current discharge between two electrodes in vacuum [2-4]. Metal plasma is produced in abundance, and it is this plasma that carries the arc current. For the work described here a repetitively pulsed vacuum arc plasma source has been used. We’ve made a number of different kinds of vacuum arc plasma guns and ion sources, from tiny, sub-miniature, UHV-compatible versions up to large, water-cooled, dc versions. Along with the metal plasma that is generated by the vacuum arc a flux of macroscopic droplets of size typically in the range 0.1 - 10 μm is also produced, and we routinely use a magnetic filter for their removal – a curved

'magnetic duct' which stops line-of-sight transmission of macroparticles while allowing the transmission of plasma by virtue of an axial magnetic field which ducts the plasma through the filter [9,10].

Metal Plasma Immersion Ion Implantation & Deposition

In metal plasma immersion ion implantation and deposition (*"Mepiiid"*) [11-13] we immerse the substrate in the metal plasma stream formed by one or more vacuum arc plasma guns while controlling the energy of the bombarding ions by the application of a high frequency repetitively pulsed bias voltage to the substrate. The ion energy can be controlled as a function of time, and the film-substrate interface can be tailored and the film structure optimized by the ion beam assist that is inherent to the process. The pulse duration is ~3 to 10 μs and the duty cycle ~10–50%. For the early stages of the deposition the pulse bias is held at a relatively high voltage of -2.2 kV. Since the vacuum-arc-produced metal ions are in general multiply stripped [9,10] and the ion energy is the product of the charge state and the accelerating voltage, $E_i = QV$, the mean ion energy can be up to 5 keV or so, with components up to near 10 keV, even for this modest voltage. At this energy ions are implanted into the substrate to a depth of up to ~100 Å. A highly mixed interface is thus produced. It is known from a large body of work on ion assisted deposition that a modest ion energy can be highly advantageous for controlling characteristics such as the density, morphology and structure of the film. For the bulk of the plasma deposition process the pulse amplitude is kept typically at around -100 V. The process has been described in more detail elsewhere [11-13].

High Energy Vacuum Arc Ion Implantation

A high current, energetic metal ion beam can be formed by a vacuum arc ion source and used to do high energy ion implantation. The ion beam is typically of diameter from a centimeter or two up to tens of centimeters, of ion energy in the range a few tens of keV up to one or two hundred keV, and of (pulsed) ion current from a few milliamperes up to several amperes. Pulse length is typically a few hundred microseconds, and the pulse repetition rate is up to a few tens or a hundred pulses per second, corresponding to a duty cycle of up to several percent. The metal ion species can be any of the solid metals of the periodic table as well as metallic compounds and alloys. Since the ions generated by the vacuum arc are in general multiply stripped, for a given extraction voltage the ion beam can have a mean energy of up to about 200 keV or more with discrete ion energy components up to about 500 keV. Vacuum arc ion sources have been used for ion implantation application by a growing number of workers at many different laboratories around the world [1,6,7]. Implantation is done in a broad-beam mode, without magnetic analysis of charge-to-mass components, and the ion trajectories are line-of-sight from ion source to target. The implantation facility developed and used at Berkeley has been described in detail previously [6,14,15]. A photograph of the source that we use routinely for our ion implantation work is shown in Fig. 1, and a large test version in Fig. 2.

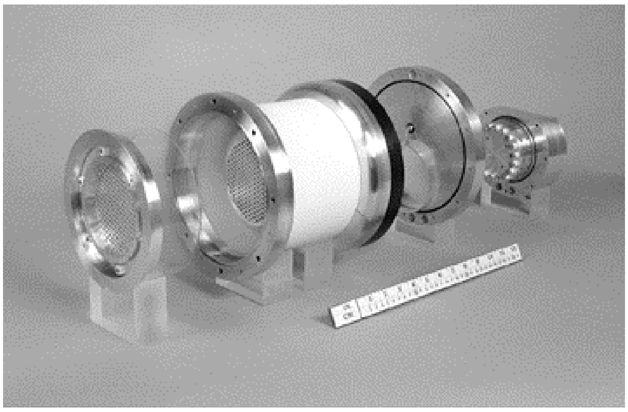

Fig. 1 The partially-disassembled Mevva V vacuum arc ion source.

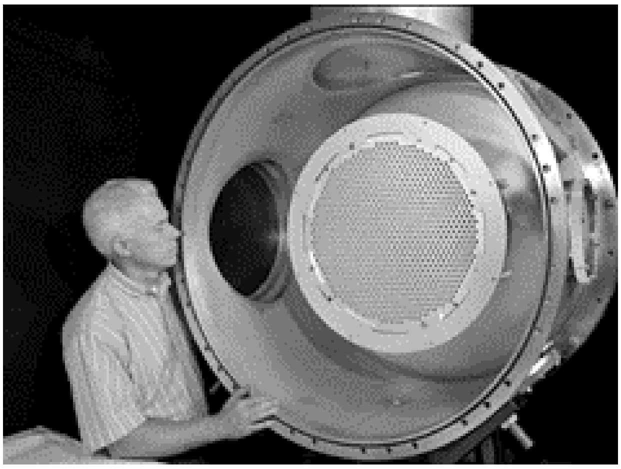

Fig. 2 50-cm diameter extractor of the ion source configuration used to form a 100 keV, 7 A (pulse) titanium ion beam.

SOME MATERIALS APPLICATIONS

A wide variety of different kinds of materials can be addressed by the techniques described here. Pure metals can be produced as deposited thin films or sub-surface layers [11,12]; by using special cathodes formed from alloys or pressed powders, films or implanted layers of metal mixtures can be made including non-equilibrium alloys [16]; by using a carbon cathode in the plasma source, films of diamond-like carbon (dlc) ("amorphous diamond") can be formed [17,18]; a gas such as oxygen can be added either to the plasma arc region or as a background gas and metal oxides (including oxide ceramics) can be synthesized [19,20]; plasmas from two or more plasma guns can be mixed in a magnetic bucket homogenizer structure to form complex mixtures of different materials [21]; by time variation of the plasma gun(s) operational mode, multilayer structures can be formed [22]; by controlling the substrate pulse bias as function of time, the interfaces between layers can be adjusted in width; and much more. In the following we describe some of the applications that we have explored.

Amorphous diamond films

When a carbon cathode is used in the vacuum arc plasma gun, carbon films are formed, and by controlling and optimizing the ion deposition energy, the film material can be in the form of diamond-like carbon (DLC), also called "amorphous diamond". Hydrogen-free DLC films have been made that are ion stitched to the substrate and with hardness up to 60 GPa, adhesion >80 MPa, density 3.0 g/cm^3 (i.e., void-free), and sp^3 (diamond bonding) fraction up to 85%. In this application, ion energy is typically held at about -2 keV in the early stages of deposition in order to achieve good film-substrate bonding and reduced to about -100 eV for most of the film growth in order to optimize the DLC properties [17,18]. The wear resistance of this material is vastly superior to that of the more conventional hydrogenated sputtered amorphous carbon films as used today for hard disk protective overlayers. Hard disks coated with 100 Å of our DLC were tested using sliders in contact at a speed of 13 m/s and a load of 40 mg. The worn volume was a factor of 20 lower for our DLC than for the sputter-coated disk. By periodically varying the carbon ion energy, multilayer structures of alternating layers of high sp^3 content and low sp^3 content DLC have been made also [23-25]. The layers of the structure are modulated in their properties such as density, hardness and internal stress. This kind of hard-soft amorphous carbon multilayered structure provides an additional degree of freedom to the film characteristics, and the overall compressive growth stress of the film can be reduced while still maintaining a very hard and wear-resistant surface. An edge-on TEM of one of our DLC multilayer structures is shown in Figure 3. We have also made DLC films and multilayer structures in which the DLC is doped with refractory metals, for example TiC/DLC and WC/DLC [21,26].

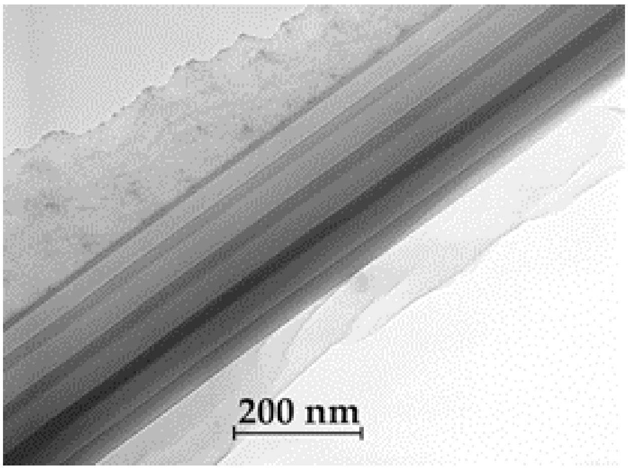

Fig. 3 Transmission electron microscope photograph of a hard/soft DLC multilayer structure.

Mullite films

Highly-adherent $3Al_2O_3.2SiO_2$ alumina-silica films that maintain their integrity and adhesion throughout repeated high temperature cycling have been made using the Mepiiid technique with aluminum and silicon plasmas in the presence of a low pressure oxygen background [20]. 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 ~100 eV (IBAD range) to optimize the film structure and morphology. The film- substrate adhesion is typically greater than ~70 MPa (the limit of measurement), and the films maintain their adhesion after repetitive cycling in temperature between ambient and 1000^{o}C. This work has been described in detail elsewhere [20].

High-Tc superconducting thin films

High-T$_c$ superconducting thin films made from an YBa_2Cu_3/Ag alloy precursor material (and post-deposition oxidation and annealing) have been made [27]. In one such experiment we formed a sandwich structure on a silver substrate consisting firstly of a plasma-synthesized Al_2O_3 buffer layer about 200 Å thick, then a YBa_2Cu_3/Ag precursor alloy layer about 1000 Å thick, capped by a Ag layer about 200 Å thick. This multilayered structure suffered from severe buckling and delamination from the substrate when 'simply' deposited, but by adding an initial high energy phase to the ion deposition the film was ion stitched to the substrate with minimal stress and excellent adhesion, and the delamination behavior was completely removed. Figure 4 shows photographs of films prepared identically except for the pulse biasing – using no pulse biasing, an intermediate value of bias, and a relatively high pulse bias.

Surface resistivity tailoring of ceramics

A technique used for the suppression of high voltage surface flashover of ceramic insulators is to provide some surface electrical conduction to bleed off accumulated surface charge. We have used metal ion implantation to modify the surface of high voltage ceramic vacuum insulators so as to provide a uniform surface resistivity of order 10^{10} Ohms per square. Our vacuum arc ion source based implanter was used to implant Pt at about 130 keV to doses of up to ~6 x 10^{16} ions/cm^2 into small ceramic test coupons and also into the inside surface of a number of ceramic accelerator columns 25 cm I.D. by 28 cm long. For implantation of the large columns, an appendage to the implanter was made which allowed the column to be continuously rotated while being implanted. A rotating cradle held the column at an appropriate angle to the incident energetic large-area ion beam while continuously slowly rotating it about its axis so that the entire inside surface was uniformly implanted (Figure 5). The mechanism was insulated and the high voltage resistance could be measured in-situ (with implantation switched off) at selected times during the processing. By appropriate choice of dose, the surface resistivity could be tailored over a range from its pre-implantation value of >10^{15} Ohms/sq. down to ~10^9 Ohms/sq. We chose to implant the columns to a dose of 2 x 10^{16} cm^{-2}. The result of this implantation processing was a significant increase in the voltage at which the column could be operated [28].

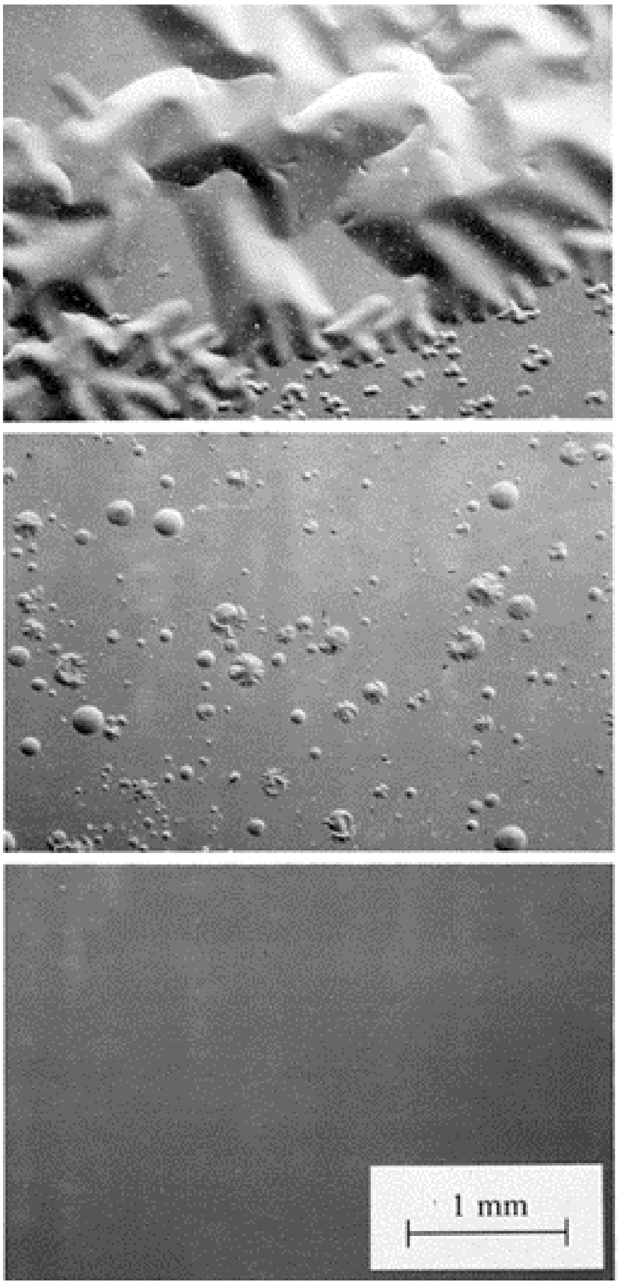

Fig. 4 High-Tc superconducting thin film (precursor alloy structures) showing the effect of pulse biasing on stress reduction and film adhesion.
Upper: No bias,
Middle: -200 V bias,
Lower: -2 kV bias.

<u>*Biomaterials applications*</u>

Biocompatible and bioactive surface coatings which can promote and stabilize cell attachment to medical instruments have been formed [29]. The coatings were made by first depositing thin films of materials such as diamond-like carbon or metals which were then further altered to either promote or inhibit cell growth and spreading by an additional overcoat of biological material. Ion energies in this case were low, of order 100 eV. These bioactive substrates have been tested on primary central nervous system neurons and the growth response is outstanding even after two weeks in culture. The method and the materials could be important in a number of areas of research and biotechnology, for example for chronic implantation of microelectrode arrays in the cerebral cortex for neuroprosthetic and neural monitoring application, and for research of the human central nervous system.

Fig. 5 Ceramic accelerator column in Mevva implanter

CONCLUSION

The metal plasma formed by a vacuum arc discharge can be utilized in a variety of ways to form thin films and modified surfaces that are of interest in many different subfields of science and technology. The essence of the techniques involves the ability to control the metal ion energy over a range of many orders of magnitude. Here we've presented a few selected examples of the materials applications investigated. Applications of metal plasma immersion ion implantation and deposition (*mepiiid*) described here include films and multilayer structures of very high quality (high sp3 and hardness) diamond-like carbon, complex ceramics, high temperature superconductors, and bioactive material applications. Mevva ion implantation applications described here include the surface resistivity tailoring of ceramics for improvement in their high voltage hold-off capabilities; other applications include rare-earth doping of semiconductors for optoelectronic applications, and hybrid metal-oxygen co-implantation of metals for tribology enhancment. Our laboratory program will continue to explore novel uses of these plasma and ion beam based surface modification tools.

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