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Thin Film Synthesis Using Miniature Pulsed Metal Vapor Vacuum Arc Plasma Guns

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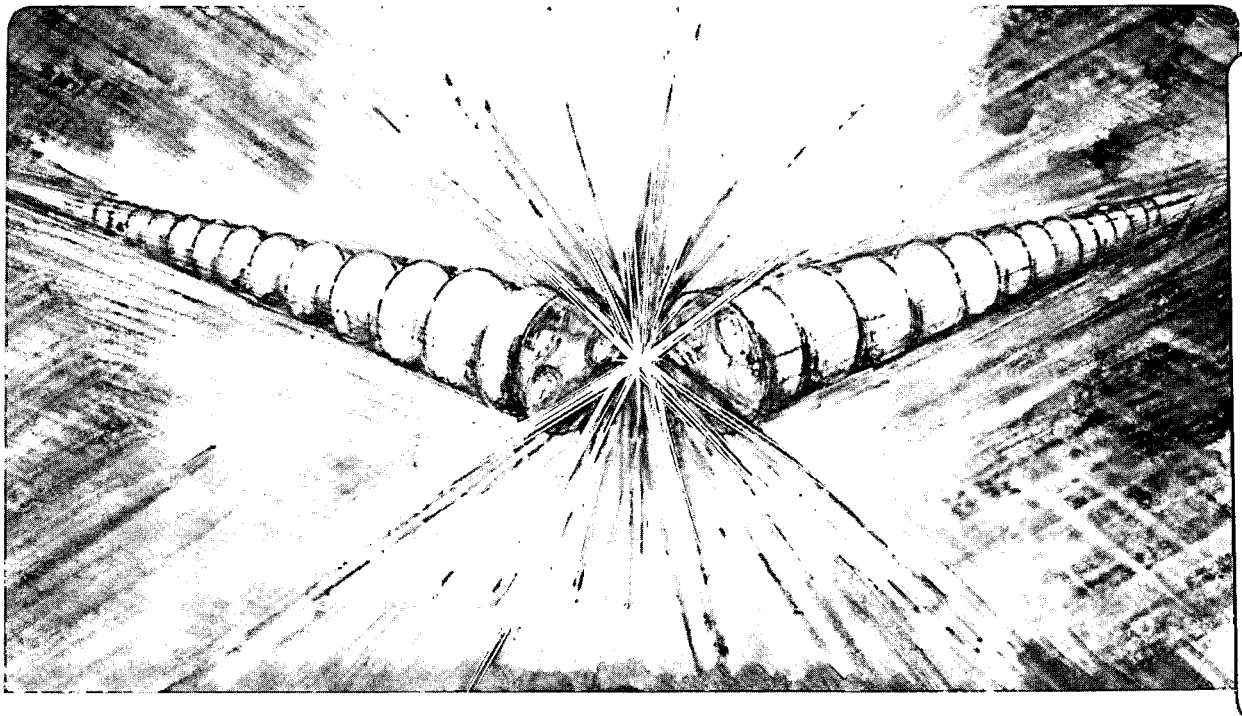

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THIN FILM SYNTHESIS USING MINIATURE PULSED METAL VAPOR VACUUM ARC PLASMA GUNS

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ABSTRACT

Metallic coatings can be fabricated using the intense plasma generated by the metal vapor vacuum arc. We have made and tested an embodiment of vacuum arc plasma source that operates in a pulsed mode, thereby acquiring precise control over the plasma flux and so also over the deposition rate, and that is in the form of a miniature plasma gun, thereby allowing deposition of metallic thin films to be carried out in confined spaces and also allowing a number of such guns to be clustered together.

The plasma is created at the cathode spots on the metallic cathode surface, and is highly ionized and of directed energy a few tens of electron volts. Adhesion of the film to the substrate is thus good. Virtually all of the solid metals of the Periodic Table can be used, including highly refractory metals like tantalum and tungsten. Films, including multilayer thin films, can be fabricated of thickness from Angstroms to microns. We have carried out preliminary experiments using several different versions of miniature, pulsed, metal vapor vacuum arc plasma guns to fabricate metallic thin films and multilayers.

Here we describe the plasma guns and their operation in this application, and present examples of some of the thin film structures we have fabricated, including yttrium and platinum films of thicknesses from a few hundred Angstroms up to 1 micron and an yttrium-cobalt multilayer structure of layer thickness about 100 Angstroms.

INTRODUCTION

The technology for the formation of thin films and compositionally modulated multilayer structures has made great advances, and an array of such techniques is available to the experimenter. These techniques include sputtering [1], electron beam evaporation [2], molecular beam epitaxy (MBE) [3], ion beam deposition [4,5], and laser ablation deposition [6,7]. There is interest in techniques for the deposition of metallic thin films also, or of multilayer structures in which one or more of the components is a metal [8-10]. The metal vapor vacuum arc [11] is a kind of plasma discharge that takes place between metallic electrodes in a high vacuum environment and that is a prolific producer of dense metal plasma. Vacuum arc plasma sources are attractive devices for the deposition of metallic thin films [12,13]. These kinds of sources produce intense fluxes of highly ionized metal plasma which when condensed form highly adherent and dense thin films. The metal vapor vacuum arc plasma discharge has been used widely for deposition of various metal coatings in a vacuum environment and for the formation of TiN protective coatings [14,15], and industrial arc source deposition equipment is readily available on the market [16]. The vacuum arc is commonly also called a 'cathodic arc'. Cathodic arc facilities are large pieces of equipment and are designed to apply metallic coatings to large substrate areas; the titanium nitriding of cutting tools and other components in a large batch processing mode is a typical application. We have taken the vacuum arc technology to the other extreme - miniature source with fine control over the deposition flux - and have thereby developed a tool which could find application for the formation of metallic thin films and multilayers over relatively small areas (though this parameter could readily be scaled up) and with thickness and composition tailoring down to the monolayer level. The method is particularly simple and inexpensive, and is well suited for thin film research involving the preparation of many experimental samples, as the set-up time required is minimal and the amount of material consumed is very small.

DESCRIPTION OF THE PLASMA GUNS

The fundamental phenomenon which drives the vacuum arc is that of cathode spot formation - minute regions of intense current concentration which reside on the surface of the cathode and at which the solid cathode material is vaporized, ionized, and injected into the interelectrode arc region. The current density at the cathode spots is of order 10^6 A/cm^2 over a spot size of order microns. A typical vacuum arc discharge might consist of from one to many dozens of such spots. A very complete review of the entire field of metal vapor arc discharges has been given by Lafferty [11] and a review of cathode spot behavior has been given by Lyubimov and Rakhovskii [17].

In the method described here, a miniature metal vapor vacuum arc plasma source is used to generate an intense flux of metal plasma in a vacuum environment. The dense metal plasma plumes away from the cathode at which it is created, through a central hole in an annular anode, and toward the substrate on which the film is to be formed. The plasma source is repetitively pulsed, and a thin film can be deposited over an area of several square centimeters in a time of several minutes.

The arc discharge is driven by a simple L-C pulse line of impedance 1 Ohm and pulse length 250 microseconds. The line is charged to a voltage of up to several hundred volts with a small dc power supply. A high voltage pulse applied to a trigger electrode initiates a surface spark discharge between the coaxial trigger electrode and the central cathode, which in turn causes the main anode-cathode circuit to close due to the spark plasma, and the vacuum arc proceeds. Typically the source is operated at a repetition rate of up to several pulses per second, a rate which is limited by heat removal considerations.

The properties of the plasma generated by this kind of plasma gun, as reflected in the extracted ion beam, have been extensively studied as part of the LBL MEVVA ion source R&D program. The MEVVA ion source has been fully described elsewhere [18-20]. The source works well with virtually all solid metals of the Periodic Table; we have operated the source and measured the ion charge state distributions using 48 different metallic elements [21,22] and a range of alloys and compounds [23].

A photograph of two slightly different embodiments of miniature plasma gun is shown in Figure 1. Both of these guns have been used.

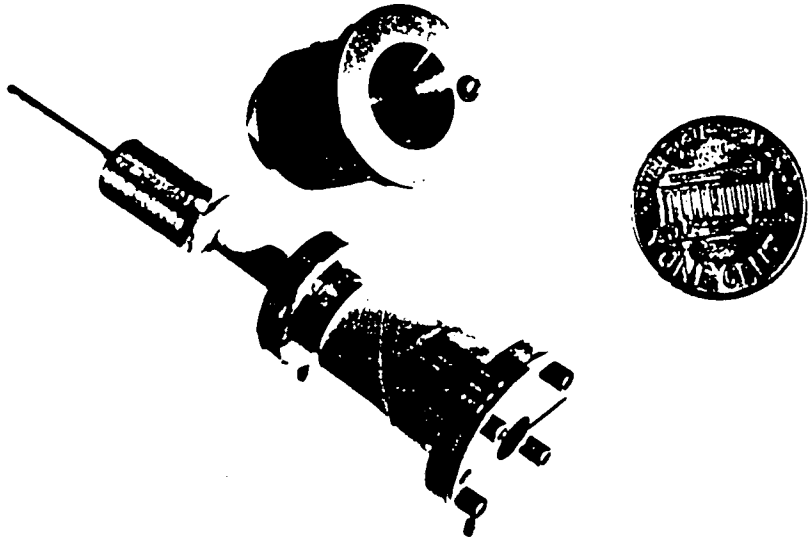

Fig. 1 Photograph of two versions of miniature metal vapor vacuum arc plasma gun.

RESULTS

In the preliminary work described here we have produced several different kinds of thin film structures on a Si substrate material. The film composition is determined by the choice of cathode metal. Films of Pt and Y were synthesized, and by using an array of two miniature plasma guns operating with different metallic cathodes we formed an alternating Co-Y multilayer structure. The guns were fired in the appropriate sequence to build up the required multilayer composition. We operated the plasma guns with an arc current of between 30 and 100 A, and the arc voltage was approximately 20 Volts. The Si substrate was biased up to -60 Volts and the plasma ion current measured at the substrate was in the range 200 mA - 1 A. The plasma gun and substrate were mounted in a large vacuum vessel with a separation distance between them of 2 -3 cm, for these experiments; this geometry produced a film of diameter on the silicon wafer of approximately 3 - 4 cm. The operating pressure was below 5 x 10^{-6} Torr. Because no cooling was provided it was necessary to operate with a low repetition rate, from about 1 pulse per 3 seconds to 3 pps. The thickness of the film was controlled by the number of shots, varied here between 1 and several thousand.

We used a number of different diagnostic methods to examine the films deposited: ex-situ RBS, SEM, TEM, Auger and in-situ XPS. A disadvantage of ex-situ methods is post-deposition oxidization of the film. The TEM data show that films 2 - 3 monolayers thick of Pt on Si were deposited by 50 pulses of the gun. In Figures 2a and 2b we show the RBS spectra obtained from a Pt film (900 shots) and an Y film (5900 shots), respectively.

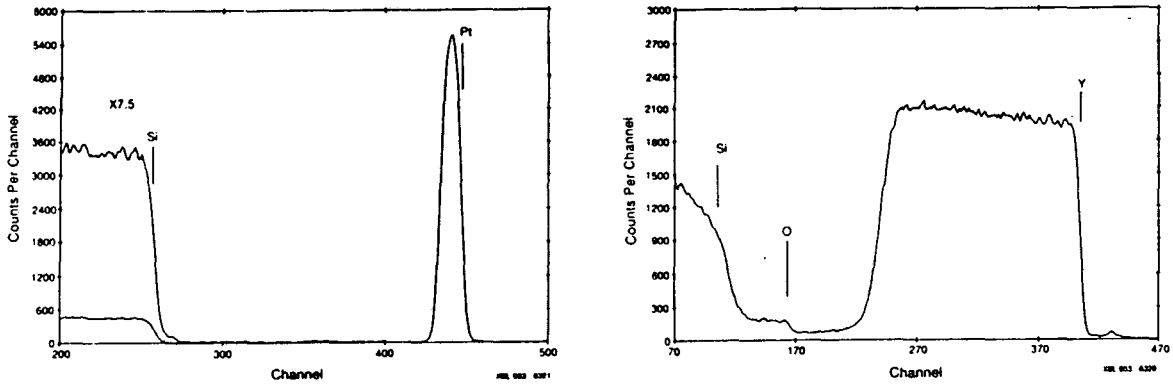

Fig. 2. RBS spectra for (a) Pt film on Si obtained after 900 gun shots; (b) Y film on Si obtained after 5900 gun shots.

The purity of the film is better than 99%. This was checked in-situ with XPS as shown in Figure 3. All the Pt peaks can be seen, and no metal impurity peaks were detected. The oxygen and carbon peaks are probably due to the use of an unclean wafer and residual gas in the modest vacuum.

Two Pt films were deposited, using 205 and 900 shots to produce doses of 2.8 x 10^{16} atom/cm^2 and 1.1 x 10^{17} atom/cm^2 (40 and 160 Angstroms thickness), respectively. The growth rate was approximately 16 shots per monolayer or 0.2 Angstroms per shot. This is in accordance with the TEM observations. With yttrium we produced a thicker film, using 5900 shots. During storage at atmospheric pressure the film oxidizes. Using RBS (Figure 2b) we measured an Y dose of 1.35 x 10^{18} atom/cm^2 and an O/Y ratio of 1.29. We can estimate that before oxidation the Y film growth rate was 5 shots per monolayer or 0.8 Angstroms per shot. Like the Pt films, the Y film is quite pure apart from oxidation.

In Figure 4 we show the Auger depth profile results for the Co-Y multilayer thin film structure. 250 shots were used to make each layer. The Co and Y layers are estimated to be 45 and 200 Angstroms thick, respectively. The interface sharpness is equal to or better than the resolution of the Auger depth profile (20Å). The deposition rate for Co is close to that for Pt (approximately 0.2 Angstroms per shot) and that for Y is the same as measured for the thicker Y layer (approximately 0.8 Angstroms per shot).

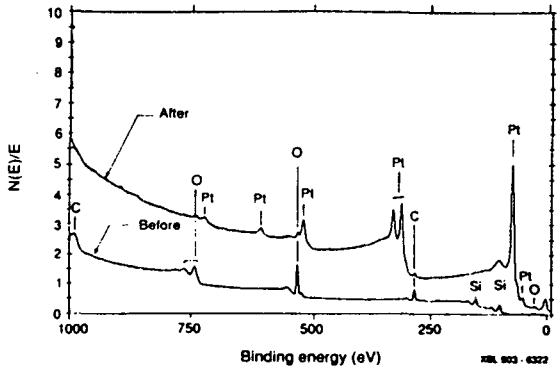

Fig. 3. XPS spectrum for a Pt film on Si obtained after 205 gun shots.

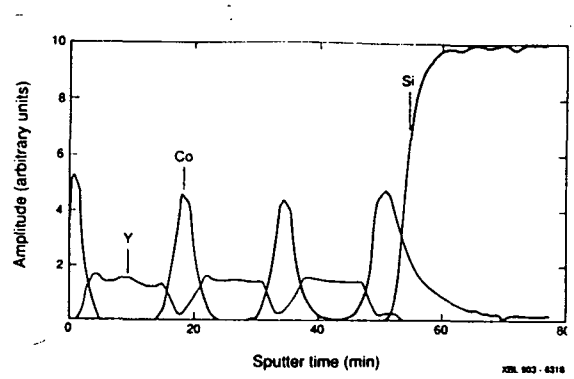

Fig. 4. Auger depth profile of Co-Y multilayer structure.

DISCUSSION

We have demonstrated that the miniature metal vapor vacuum arc plasma gun described here provides a valuable tool for the synthesis of metallic thin films and multilayers. Operation in a pulsed mode permits control of the film deposition to within a tenth of a monolayer, or much less by appropriate choice of geometry. The synthesis of films of monolayer or sub-monolayer thickness is simple and can be done in a matter of minutes or less. Films of thickness a few tenths of a micron can also be formed. It has been established in related work [21,22] that the plasma gun operates well with nearly all the metallic elements of the Periodic Table, and it is possible to synthesize thin films and multilayers of any metals or any combination of metals. Alloys, chemical compounds, and some semiconductors can also be employed [23]; we have for example used - stainless steel, brass; FeS, PbS, TiN, SiC, WC, UC; Si, C.

Because of the directed energy of the plasma stream (typically several tens of electron volts), film adhesion to the substrate or adhesion of interleaving multilayers to each other is good. That the deposition flux is pulsed and that the timing of the plasma pulses can be controlled to the microsecond level could provide a means for carrying out some novel experiments. For example, highly reactive films can be deposited and immediately covered with another film. By using two plasma guns operating simultaneously it should be possible to form novel non-equilibrium materials. Finally, because the deposition flux is in the plasma state and contains multiply charged and highly excited ions, some novel chemistry effects might be expected and could perhaps be harnessed.

Along with the metal plasma that is generated there is also a flux of macroscopic droplets, of size typically in the broad range 0.1 - 10 microns [24-26]. We have examined the films prepared here under SEM and have found a small but real 'macroparticle' contamination on the film surface (Fig.5).

The origin of these particles is at the cathode spot itself and results from the intense heating of the cathode material beneath the spot. A volume of material is rendered molten by the arc and the pressure gradient in the vicinity of the arc expels molten droplets along with the vapor. The volume of molten material formed is less for higher melting point materials, and the macroparticle contamination is observed to be less for cathode materials of higher melting point. For some applications, useful films can be made by proper selection of cathode material. In the case of a carbon cathode (and also some other elements and compounds), even larger solid particles are ejected from the arc spot. These result from the porous nature of most solid carbon materials. Gas trapped in voids in the cathode causes pressure gradients which blow solid pieces of cathode from the source.

There is a natural separation of the wanted plasma flux from the unwanted macroparticle flux by virtue of the fact that the plasma flux is peaked in the direction normal to the cathode surface while the macroparticle flux is peaked in a direction close to parallel to the

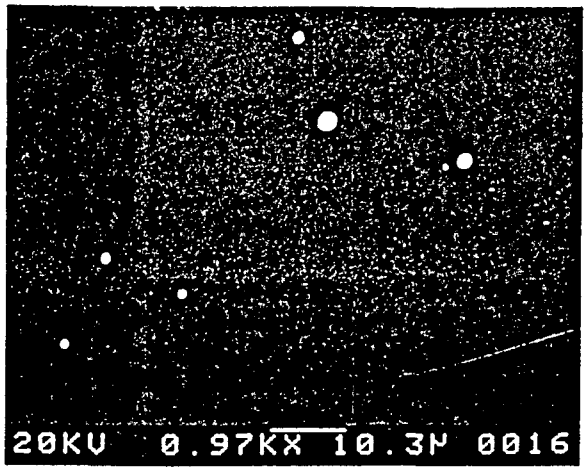

Fig. 5. SEM micrograph of macroparticles lying on a Pt film.

cathode surface. For those applications for which the macroparticle generation is severe or for which absolutely particle-free films are required, a magnetic filter can be used, as has been described by several workers [27-29]. The macroparticles travel in approximately straight line trajectories from the cathode because their velocities are quite high, up to 800 m/sec [30]. An effective filter is thus an optically dense channel which permits plasma transmission with good efficiency. One simple configuration, that could be suitable for some applications, is a curved tube or pipe which precludes line-of-sight macroparticles from passing through it, while allowing a relatively high transmission of plasma by virtue of an axial magnetic field which ducts the plasma through the filter [27,31-33]. There is in general a loss of plasma through the filter and a consequent decrease in deposition rate at the other end.

We are presently developing a device with which we will be able to form multilayers composed of up to 10 different metal species in a single batch. This thin film synthesis device will include 10 cathodes and a rotating substrate holder. We will be able to make, for example, high-Z/low-Z multilayer structures and Y-Ba-Cu structures with each layer from a few Angstroms to several tenths of microns.

CONCLUSIONS

We have developed and tested a miniature metal vapor vacuum arc plasma gun. Preliminary results demonstrate the ability of this device to control the growth of metallic thin films very accurately, to within a few tenths of an Angstrom, of thickness from sub-monolayer up to microns. It is possible to produce films of nearly all the metallic elements of the Periodic Table. Using an array of such guns, multilayer structures of a wide range of metallic components can be fabricated.

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