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CHARGE INJECTION PROPERTIES OF IRIIDIUM OXIDE FILMS
PRODUCED ON Ti-6Al-4V ALLOY SUBSTRATES
BY ION-BEAM MIXING TECHNIQUES

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CHARGE INJECTION PROPERTIES OF IRIIDIUM OXIDE FILMS PRODUCED ON Ti-6Al-4V ALLOY SUBSTRATES BY ION-BEAM MIXING TECHNIQUES

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Summary

The charge injection capabilities of iridium oxide films, as produced on Ti-6Al-4V alloy substrates by ion beam mixing techniques, have been investigated. Iridium oxide is a valence change oxide, and therefore has high values of charge injection density upon voltage cycling in electrolytes. Because of this property, iridium oxide films are useful as working elements in neural prostheses. Iridium films of three thicknesses, produced by sputter deposition followed by ion beam mixing, were tested in cyclic voltammetry out to 1000 cycles or more. Two surface preparations, mechanical polishing and an acid passivation treatment, were also used as controls. Surface analysis was primarily by Rutherford backscattering spectrometry. Both the ion-beam mixing and the acid pretreatment increased the lifetimes of films, in comparison with the mechanically polished standards. Reductions in charge injection capability, when they occurred, were attributed to loss of Ir from the films, and there was a close correlation between the charge injection density and the Ir inventory.

1. Introduction

When iridium oxide is cyclically polarized in a suitable electrolyte and over a suitable range in potential, changes in oxidation occur, which lead to high charge injection values. The reversible reaction responsible for the effect is thought to be [1]:

Thus, during the anodic portion of the cycle, $\text{Ir}(\text{OH})_3$ goes to $\text{IrO}(\text{OH})_2$, corresponding to a valence change from Ir^{3+} to Ir^{4+} , with the release of a proton and an electron. During the cathodic portion the reverse reaction takes place. The valence transition occurs within potential limits less than are required to electrolyse water. In part because of this property, and also because of the high resistance of iridium oxide to dissolution in corrosive media, iridium oxide has emerged as a candidate material for the working element in certain devices. Perhaps the most important among these at present are charge injection electrodes for stimulation of nerve tissue (neural prostheses [1]). Biocompatibility of the oxide surface is also an important factor for this application. In addition to charge injection capability, the oxide is interesting because of electrochromism [2]. The higher oxidation state has a blue color. There has also been interest in use of the oxide as a pH detector [3].

For combinations of reasons that will not be discussed, full exploitation of the properties of iridium oxide in conjunction with modern device technology is likely to depend on the ability to produce stable films of Ir (and its oxide) on different kinds of substrates-insulating, semiconducting, and metallic. Previous research by the present authors has developed one method of coating Ti or Ti-6Al-4V with Ir [4,5,6]. In that method, the Ir was directly implanted into the alloy by high energy ion implantation. Then the Ir was precipitated onto the surface from underneath by use of a severe corrosion

treatment, which removed base alloy constituents but not the Ir. It was believed that such a film would probably be the most adherent and laterally uniform type of film that could be produced. Nevertheless, it was also suspected that the method might have design limitations, in that it might be difficult to produce films with given values of charge injection, at least without considerable trial and error [6].

The present experiment has investigated high energy ion-beam mixing of Ir films that had been sputter deposited onto Ti-6Al-4V alloy substrates. The purpose was to explore parameters, performance and reasons for success or failure of these methods. The Ti-6Al-4V alloy is a rugged, corrosion resistant, and biocompatible alloy, which might be useful for construction of some devices. Presumably, results of the present study would be readily extendable to commercially pure Ti. Titanium and its alloys also find use in orthopedics, artificial heart construction, and other biomedical applications where enhanced corrosion protection due to Ir might be a benefit.

2. Experimental Procedures

2.1 Sample preparation and processing

Alloy coupons were prepared for sputter deposition of the Ir films in two ways. The first was a mirror-like mechanical polish produced by use of an alumina compound followed by finishing with colloidal silica. For the second, this polishing treatment was followed by a passivation treatment that consisted of immersing the sample in a solution of 50 vol % concentrated HNO_3 (70.2 wt. % HNO_3) in distilled H_2O at 50°C for 30 min. The reason for the passivation treatment was that IrO_2 and TiO_2 have the same crystal structure [7]. It was conjectured that a chemically formed passive oxide coating might serve as a better template for adhesion of the iridium oxide than the polished metal. The

intent was to compare possible advantages due to ion-beam mixing to two possible other standard surface treatments. This procedure was followed in part to avoid overstating advantages of ion-beam mixing because of fortuitously obtaining only the most favorable comparison among possible competing surfaces. Processing steps for the respective kinds of samples, including control samples, are described qualitatively in Table I.

TABLE I

COMBINATIONS OF PROCESSING STEPS USED FOR RESPECTIVE IR-FILM SAMPLES
ON Ti-6AL-4V SUBSTRATES

-
1. Mechanical polish only + Sputter deposition of Ir.
 2. Mechanical polish + Passivation + Sputter deposition of Ir.
 3. Mechanical polish only + Sputter deposition of Ir + Ion-beam mixing.
 4. Mechanical polish + Passivation + Sputter deposition + Ion-beam mixing.
-

Iridium films were sputter deposited onto the alloy coupons by use of a Hummer 21042 system by Technics, Inc. Nitrogen ions were used. The current was 10 mA, the voltage was 2.5 kV, and the pressure was 100 mTorr. The deposition rate was not precisely known at the outset. Three thicknesses of films were produced, corresponding to 3, 5, and 8 minutes of sputtering time. Analyses to be presented demonstrated that the respective thicknesses were 6.6, 11.8, and 18.8 nm.

Ion-beam mixing was done by use of Ti beam ions produced by a Varian/Extrion 200–1000 implanter, a well-known commercial unit, which provides for magnetic analysis of the beam. For the respective thicknesses of Ir films, suitable beam parameters were estimated by calculation (TRIM [8] and PROFILE [9]) to produce the desired mixing, consistent with an acceptable level of sputtering of the film from the substrate. Energies of Ti ions were 50, 100, and 150 keV for the respective thicknesses of Ir. The energies were chosen to produce average ranges somewhat greater than the Ir film thicknesses and maximum energy depositions at/near the interfaces between films and substrates. For the implantations, the samples were firmly secured to a Ni-block sample holder of some 500 g in mass, which was precooled to about 0 °C before the beam was turned on. All doses were $1 \times 10^{16}/\text{cm}^2$, and for these low doses, the heat capacity of the precooled block assures freedom from excess beam heating. Characterizations of these processing results by Rutherford backscattering spectrometry (RBS) analysis will be presented.

2.2 Other techniques

Analyses of samples by RBS [10] were performed for each sample at various points in the procedure as needed to determine Ir inventory, depth distribution changes for Ir, sputtering coefficients and other pertinent information for the process. All analyses were done by use of 2.0 MeV He ions at a backscattering angle of 160°.

After preparation by one of the procedures indicated in Table I, the samples were “activated” by repeated cycling to a few hundred potentiodynamic cycles in 0.1 M H₂SO₄ solution. This repetitive cycling apparently adds progressively more oxygen for each cycle until a saturation level is reached such that three oxygen atoms for each Ir atom in the oxide layer exist. Charge injection by the reaction given above increases until this point of saturation is reached. Thereafter, reversibility apparently exists unless Ir is lost from the

surface. It had been found by the present authors and others [11] that activation was faster in H_2SO_4 than in saline. Voltage limits for the scans were 0 to 1.4 V versus the standard hydrogen electrode (SHE). The wave form was a linear ramp up and down at a scan rate of 100 mV/s. After activation was complete, cycling was continued up to 1000 or more cycles to ascertain long-term stability of the films under cycling. The stability of the charge injection under this continued cycling provides one basis for judging merit in the present experiments.

2.3 Characterization of sample processing results

Figure 1 shows RBS histograms for two samples with the thinnest layers (6.6 nm thick) of sputter-deposited Ir. One sample had been passivated before deposition and the other had the mechanical polishing treatment only. The most important point is that the amount of oxygen on the passivated sample does not exceed that on the sample which had been polished only. Because of the small scattering cross section, the oxygen peak is quite small, but it can nevertheless be estimated that the surface density of O for the mechanically polished sample did not exceed about $2 \times 10^{16}/\text{cm}^2$. It might be noted from Fig. 1 that these small peaks for O are hardly more pronounced than many of the statistical variations due to scatter in the data, which are left uninterpreted. Mass resolution for the He-ion RBS technique in this mass range is excellent, however. A limited interpretation is possible because the energy position of these peaks is accurately known, and the scattering yield, though small, can be quantitatively predicted with good accuracy for given proposed surface concentrations of O. The same applies for carbon, which will be mentioned in the discussion. Each sample was analyzed, and in no case was oxygen more apparent on a passivated sample than on a mechanically polished one. Thus, whatever the passivation treatment did, it apparently did not thicken the oxide appreciably. The Ir peaks and the Ti edges will be interpreted with the aid of Fig. 2.

Figure 2 presents histograms for a sample with the 11.8 nm-thick layer of Ir, before ion mixing and after ion mixing. Also, a histogram for a bare alloy substrate is presented. Because of energy loss as the He analyzing beam passes through the deposited Ir, the Ti edge is suppressed to a lower energy for the coated sample than for the bare sample. The breadth of the Ti edge, being determined primarily by spectrometer resolution, remains the same for the Ir-coated as for the uncoated sample before ion mixing. By use of He energy loss data, the thickness of the Ir film can be determined by the energy offset of the Ti edge for the as-deposited films. For the ion-beam mixed samples, the Ti edge has been broadened. At the lower energy a departure from the plateau level is detected at about the same energy as for the as-deposited sample. At the higher energy, a tail reaches out far enough to merge with the curve for surface Ti. The Ir peak has been modified in two ways. First, the area has been reduced due to sputtering by the ion-mixing beam. Second, in normalized form, the peak has been broadened, particularly on the backside (low energy). This broadening represents inclusion of Ir within the Ti substrate and inclusion of Ti within the film. Iridium films were not thick enough to allow determination of thickness by differences in backscattered He energy from Ir atoms on the front side and the back side of the film, for our spectrometer resolution. Thickness could be derived by comparison of the total RBS counts from the Ir with total counts from a given thickness of substrate. Thus, there were two ways of determining film inventory, total Ir counts and Ti-edge offset. The latter was not useful for ion mixed samples, however, because of broadening of the Ti edges.

Table II summarizes these processing results. The Ir thickness determinations are in fair agreement with each other for the two methods for the thinnest layer and progress to excellent agreement for the thickest. The thicknesses determined by total RBS counts are preferred because these values correlate better with the sputter times and also are the only

ones that are useful throughout the whole experiment. The reason for the disagreement is not known. On the whole, for the three thicknesses of films, the ion-beam mixing design produced approximately the results that were expected. Intermixing over depths approximating the initial thicknesses of the films was produced, as is evidenced by the fact that some Ti counts were detected due to Ti atoms all the way out to the Ir surface.

TABLE II
ION BEAM MIXING PARAMETERS AND RESULTS

Ir Thickness from Ir RBS Counts (nm)	Ir Thickness from Ti Offset (nm)	Ir Surface Atomic Density from RBS counts ($10^{16}/\text{cm}^2$)	Energy of Ti Mixing Ions (keV)	Calculated Range in Ir (nm)	Remaining Ir Surface Atomic Density ($10^{16}/\text{cm}^2$)	Y, Sputter Coefficient
6.6	9.6	4.6	50	15.0	3.2	1.4
11.8	14.8	8.3	100	27.7	6.2	2.1
18.8	19.8	13	150	40.5	11	2.2

3. Results

Figure 3 shows cyclic voltammograms as measured at intervals of 100 cycles for cycling up to 500 cycles for the sample of 6.6 nm nominal initial Ir thickness that was passivated and ion-beam mixed. These curves illustrate the typical form of the raw data. Since the potential-versus-time curve is linear (100 mV/s), the half-area for the anodic (positive current) side of one of these curves is proportional to the charge that has been transferred to the auxiliary electrode during the anodic portion of the cycle. We refer to the charge corresponding to this half-area as the charge injection. In addition to stability,

another criterion for performance is charge density, i.e., charge injection per unit of sample area. For this sample, the charge injection has increased to a peak value in the neighborhood of 300–400 cycles. By 500 cycles, there is a slight decrease in area of the curves, as is reflected by the fact that the onset of high current on positive polarization does not occur until a higher voltage for the 500 cycle than for the 400 cycle. It is suspected that this shoulder or satellite peak may be due to the irreversible addition of oxygen, which builds up inventory of $\text{Ir}(\text{OH})_3$ on each cycle. Most of the area is apparently due to the reversible reaction, however. Although the raw data are not shown, there is a continual gradual decrease in charge injection for this particular sample out to 1000 cycles.

These histories and detailed shapes of the curves are not the same from one sample to another, however. The type of plot shown in Fig. 4 provides a more convenient way of comparing results from one sample to another over the 1000-cycle history. These curves represent the charge injection (mC in the half-area) per cm^2 of sample area divided by the number of Ir atoms per unit area (in units of $10^{16}/\text{cm}^2$), versus number of cycles. Thus, the units on the ordinate are $\text{mC}/10^{16}\text{-Ir-atoms}$, and the normalization is for the number of Ir atoms in the surface at the start of the test. Absolute values of charge injection density can be obtained by multiplying the ordinate values by the surface Ir atomic density given at the top of the graph for each sample. Normalization of results in this way allows ready comparison with the ideal charge injection of 1-electron/Ir-atom for the valence transition of 1. The curves of Fig. 4 are for the 11.8 nm nominal thickness. Most of the differences in starting values of Ir for the ion-beam mixed samples, in comparison with the one that was passivated only, are due to sputtering during ion-beam mixing. A reduction in the apparent value of $\text{mC}/10^{16}\text{-Ir-atoms}$, such as occurred for the “as-polished + ion-beam mixed” sample after about 800 cycles, is interpreted as being due to a loss of Ir from the film during repeated cycling. In this case the loss was from $6.2 \times 10^{16}/\text{cm}^2$ to $1.1 \times 10^{16}/\text{cm}^2$ at the end. This loss of Ir is an undesirable result.

It will be noticed that for the 11.8-nm set of curves of Fig. 4 there is no curve for the sample that was only polished before sputter deposition of the Ir. The reason is because the lifetime was so small for that type of control sample. The films on the as-polished substrates only lasted about 300 cycles, and in fact were so unstable that a high level of activation could not be realized. The Ir was coming off at the same time that activation was going on. Thus, referring again to Fig. 4, even though the as-polished + ion-beam mixed sample did not last as long as either of the passivated samples, the result nevertheless demonstrates that ion mixing has a very favorable effect for the samples that were polished only. This result was true for all three thicknesses, since the lifetimes for the as-polished samples were all rather small.

For the other two sets of starting thicknesses, curves of the types shown in Fig. 4 varied in some detail. For example, the "passivated only" sample of Fig. 4 was the only one that showed the early maximum, followed by the long flat region. Nevertheless, there were common features, and a partial qualitative summary of the results is given here:

- For the polished samples, ion beam mixing produced considerable enhancement in number of cycles in the effective lifetime. Nevertheless, appreciable loss of Ir occurred by about 800 cycles, even for the ion-beam mixed samples.
- For the passivated samples and the passivated samples that were ion-beam mixed, stability was quite good out to 1000 cycles or the duration of the test, which sometimes was greater. In terms of stability, there was no clear improvement due to ion-beam mixing in comparison with the passivation treatment by itself.

- It required more cycles to achieve a peak or plateau level of activation for the ion mixed samples than for the others.
- There was a tendency for ion-beam mixing to produce some enhancement of specific charge injection per Ir atom, as is shown in Fig. 4.

Results will not be presented graphically, but it was clear from the RBS analyses of activated samples that O was added to the surface by the activation process, as expected. There were reductions in backscattering yield per unit of energy loss for Ti and Ir because of additional inelastic losses contributed by the oxygen. In addition the scattering due to oxygen increased.

Figure 5 shows charge injection densities (mC/cm^2) for the collection of samples versus surface atomic density of Ir. For these data the maximum values in charge injection (see Fig. 4 for example) were identified with the starting values for Ir surface concentration, and end values for charge injection were identified with end values for Ir surface concentration. The correlation with the 1-electron/Ir-atom criterion is rather good, indicating that for this scan rate, and up to the maximum thickness of these films, every Ir atom presumably undergoes the valence transition. The reasons for scatter in the data are not precisely known. It is not surprising that, relative to this fixed line, most of the scatter is positive. Any double layer capacitance effects would be expected to make a positive contribution. Moreover, as was noted above, ion-beam mixing apparently enhances the specific charge injection to some extent. This trend is evident by examination of the points in Fig. 5. Errors that produce scatter in RBS analysis of Ir concentration are most likely related to non-uniformities in Ir distribution, since delamination tended to occur in patches. The analyzing beam was 1 mm in diameter, but the charge injection was for the whole

surface. It would be interesting to perform this correlation by use of a more extensive analytical survey of all of the surface area.

Absolute charge injection performance can also be discussed conveniently with the aid of Fig. 5. The highest value of charge injection density achieved was about 24 mC/cm^2 , this point being the triangular shaped one at about $11 \times 10^{16}/\text{cm}^2$ of Ir. This value was the maximum for that sample, but was not stable. As noted above, much of the Ir eventually came off for samples that were as-polished and ion-beam mixed. In fact, the lowest point on the graph (near the origin) is for that same sample after most of the Ir came off at some 800 cycles. The highest stable value on the graph is the square point at about $10 \times 10^{16}/\text{cm}^2$ of Ir and 20 mC/cm^2 of charge injection. This value is for the sample that was passivated and ion-beam mixed, of the nominal initial thickness 18.8 nm. Unfortunately the sample of the same thickness that was passivated only was accidentally destroyed, but based on the rest of the data in this experiment, performance would presumably have been about the same as for the ion-beam mixed sample. As far as the ultimate charge injection that could be achieved is concerned, no design limit has apparently been reached, since the curve of Fig. 5 remains essentially linear for the thicknesses spanned. This statement might not necessarily be true for higher frequencies of scanning, however.

4. Discussion

As has been pointed out [12], the three main factors affecting performance of films, for corrosion processes (in contrast to wear) are porosity, adhesion, and stress. For the present films, stress might be a factor because the volume change during activation (addition of oxygen) might make the film tend to be in compression relative to the substrate, and thus to bow up and/or crack. Ion mixing might improve performance in this

regard by diffusing the stress field at the interface over a broader range of depths and also by improving adhesion. This effect might explain the better performance for the ion-beam mixed, as-polished samples. For the same surface preparation, ion mixing might also produce improvement if porosity of the initially deposited Ir film were a factor. The good adhesion and alloying effects produced by ion mixing could help reduce corrosive undercutting and the resulting spalling initiated at pores and cracks.

The most surprising result of the present experiments, however, was that the passivation treatment was as effective as it was in improving the stability of the films. This is especially true in view of the fact that the passivation treatment had little apparent effect in thickening the oxide. Presumably the oxide layers, of thicknesses no greater than about 5 nm, would remain amorphous [13]. Thus the idea that the crystalline TiO_2 might provide a better template for the iridium oxide is probably not true. Carbon is often found in the makeup of air-formed oxides on Ti [13 e.g.]. Carbon and Ir have a repulsive chemical interaction with hardly any mutual solid solubility at low temperatures. It might be suspected that the strong acid passivation treatment could remove the C or other contaminants. Another possible effect could be a change in character of the oxide. Air-formed oxides do not contain hydrogen, but the passivation could produce an oxide containing OH^- . Such an oxide might be more wettable by deposited Ir than air-formed oxide. As far as the possible carbon contribution is concerned, present data, though not conclusive, do not support this view. Small carbon peaks were sometimes detected by RBS, but again there were not systematic differences between the polished and the passivated samples. It is also known to be difficult, even with relatively clean vacuum processes, to avoid contamination of Ti surfaces with C. Therefore, it is possible that C was cleaned off by the passivation process, and the samples were recontaminated during the Ir deposition process. Future research in this area should make use of other surface analytical techniques that are more sensitive to light elements.

Adhesion, wettability, and porosity are undoubtedly closely connected issues, but given that ion mixing by itself did not produce perfect results, there is reason to suspect that the passivation treatment may have worked, essentially, by reducing porosity of the as-deposited Ir, instead of improving adhesion. In addition to the factors mentioned above, the strong acid treatment, performed as it was, shortly before the Ir deposition process, may have removed particles, thicker air-formed oxide patches (perhaps Al_2O_3), residual particles of polishing compound, etc., that would not have been removed by the organic solvent wash used for the mechanically polished samples. These effects may have manifested themselves in improved adhesion, more wettability, or a less columnar structure, but the most important manifestation, in comparison with the mechanically polished samples could be less porosity. Micrographs of the surfaces for a few of the samples were made after sputter deposition. Further inspection of these has revealed that Ir coatings on polished samples were considerably more porous than for the passivated samples. These results illustrate the importance of controlling every detail of film production, if the application involves corrosion processes.

Further analyses are needed to answer many of these questions. Meanwhile we judge that the present data are most compatible with the following tentative hypotheses:

- Stresses due to activation alone are not great enough to delaminate reasonably adherent films (e.g., those produced after passivation).
- The HNO_3 acid treatment (so-called passivation) reduces porosity of the as-deposited Ir film by providing an important cleaning function just before film deposition or by producing a hydrogen-containing oxide which is more wettable than the air-formed oxide, or both.

- Ion-beam mixing improves adhesion and serves to decrease the consequences of porosity for corrosive situations.

The reason for the tendency towards increased charge injection for ion-beam mixed samples is not known. Since the extra charge injection appears to be over and above that which is accounted for by 1-electron/Ir-atom, it is presumed that increases in effective surface area, cracking, or any other processes that would facilitate involvement of more Ir atoms, are not the reason. Moreover, the possible contribution of an irreversible component due to addition of oxygen cannot be discussed in detail for the entire set of thicknesses and histories that has been surveyed in the present experiment. This irreversible contribution, represented perhaps by the smaller current peak at about 0.6 V (Fig. 3), would presumably saturate after three atoms of O had been added for each Ir atom. Separation of effects due to irreversible addition of oxygen and the reversible reaction cited above is a goal of future research.

In part for reasons given in the previous paragraph, the increase in charge injection for the ion-mixed samples is not necessarily seen as a practical advantage at present. In addition, the design limit for charge injection density for samples as prepared by these methods was apparently not reached in these experiments, as was noted above. Also the cycling frequency used in the present tests was rather low, and data for higher frequencies are needed to ascertain performance for many applications [1]. For cycling in acidic rather than saline solutions, it may be that the ready availability of H^+ ions improves the kinetics.

Continued testing in the corrosive H_2SO_4 , after activation, may amount to an overly severe test, relative to what is needed to assure adequate performance in the milder saline solution. Nevertheless, stringent testing is often necessary to resolve real differences, and

we note that these tests have still not resolved any differences in stability between the ion-mixed plus passivated samples and the samples which were passivated only. This result does not imply that ion mixing would not have any effect under a still more severe test, mechanical or chemical.

In comparison with the previous procedure [4,5] of direct ion implantation coupled with a corrosion treatment to precipitate the implanted Ir at the surface, we have pursued the present line of research because we thought the present procedure would be more designable on the basis of existing data, require less development, and produce devices with higher ultimate charge injection capability. One advantage to the direct ion implantation process, however, is the near absence of lateral variation (porosity) and high degree of quality control inherent in the direct ion implantation process.

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Figure Captions

- Fig. 1. RBS histograms for as-polished and for passivated Ti-6Al-4V alloy substrates that have been sputter deposited with the thinnest layer of Ir that was used (6.6 nm).
- Fig. 2. RBS histograms for a bare Ti-6Al-4V substrate, a substrate that has been deposited with Ir (11.8 nm) and for one that has been deposited with 11.8 nm and then ion-beam mixed.
- Fig. 3. Cyclic voltammograms for the sample of 6.6 nm thickness that was passivated and ion beam mixed. The electrolyte was 0.1 M H_2SO_4 . The inner loop is for the tenth cycle. Thereafter, loops are for the 100th, the 200th, etc. up to 500 cycles. Testing was continued to 1000 cycles.
- Fig. 4. Charge injection for 10^{16} starting Ir atoms versus number of cycles in H_2SO_4 for the set of samples of nominal intermediate starting thickness (11.8 nm).
- Fig. 5. Charge injection density versus surface atomic density of Ir for the collection of samples.

6.6-nm Sputter Deposited Ir

Fig. 1.

11.8--nm Sputter Deposited Ir

Fig. 2.

Sample 12, after Ion Beam Mixing, H_2SO_4 .

Fig. 3.

Fig. 4.

Fig. 5.

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