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# Application of filtered pulsed vacuum arc plasma to deposite $Al_2O_3$ thin films

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In this study, we report our recent work using pulse metal vacuum arc to synthesize $Al_2O_3$ thin films. $Al_2O_3$ thin films were deposited on Si(100) and glass substrates by using filtered pulsed vacuum arc plasma of aluminum in the atmosphere of oxygen gas. The fabricated thin films were characterized by using transmission electron microscopy, scanning electron microscopy, atomic force microscopy and glancing angle incident x-ray diffraction to reveal their crystalline quality, morphology, and grain size. The chemical composition and bonding characteristics of the thin films were determined using Rutherford backscattering spectrometry and x-ray photoelectron spectroscopy. The properties of thin films, such as adhesion strength to the substrate, hardness, transmittance, refractive index, were also evaluated.

## I. INTRODUCTION

The concept of plasma immersion ion implantation (PIII), or plasma source ion implantation (PSII) was first proposed by Conrad *et al* in 1980s[1]. Since the advantages of PIII over the traditional line beam ion implantation, PIII has been rapidly developed and widely applied to enhance the surface properties of materials. Metal plasma immersion ion implantation (MPIII) was also established based on the idea of PIII. In the past several years, extensive progress has been made in understanding the improvement of the mechanical properties of the treated materials, but there were few reports on the synthesis of functional materials by this technique.

Aluminum oxide ($Al_2O_3$) thin films are potential candidates in optoelectronic and microelectronic applications because of their excellent properties such as high temperature chemical stability, high electrical isolation, and thermal conductivity[2-6]. Due to their high hardness, they can also be employed as protective and passivating coatings[7]. In the past years, a wide spectrum of deposition technologies has been employed to synthesize $Al_2O_3$ thin films, including reactive magnetron sputtering (RMS)[8], metal organic chemical vapor deposition (MOCVD)[9], plasma assisted molecular beam epitaxy (MBE)[10], pulsed laser ablation deposition (PLD)[11], and ion beam assisted deposition (IBAD)[12]. Among these techniques, PLD is cited to have advantage over others because it can stoichiometrically transfer the target composition to the films with a higher energy (5-20 eV) of the ablated species at a higher partial pressures of reactive gases. However, laser ablation needs a particular target material and cannot uniformly grows thin film on substrate in enough large area.

In this study, we report our recent attempt by using pulse metal vacuum arc to synthesize $Al_2O_3$ thin films. $Al_2O_3$ thin films were deposited on Si(100) and glass substrates by using filtered pulsed vacuum arc plasma of aluminum in the atmosphere of oxygen gas and were characterized by using transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM) and glancing angle incident x-ray diffraction (GIXD) to reveal their crystalline quality, morphology, and grain size. The chemical composition and bonding characteristics of the thin films were determined using Rutherford backscattering spectrometry (RBS) and x-ray photoelectron spectroscopy (XPS). The film properties, such as adhesion strength to the substrate, hardness, transmittance, refractive index, were also evaluated.

## II. EXPERIMENTAL

### A. Synthesis of $Al_2O_3$ thin films

The growth experiments of $Al_2O_3$ thin films were carried out in the MPIII system that was developed at City University of Hong Kong. Figure 1 is the schematic of the system. The system consists of 4 pulsed filtered cathodic arcs and a radio frequency gas plasma source. There are also some assisted thermal filaments to generate plasma. DC or pulsed high voltage can be applied to the target. The arc source generates an intense, pulsed highly ionized Al plasma plume with a characteristic velocity of $1\text{-}2\times10^4$ m/s. The peak arc current was about 110 A. The pulse frequency was 25 Hz and the pulse duration was 300 μs, which corresponding the deposition rate of 0.05 nm/s for Al. A DC voltage of 150 V was applied to the target. $Al_2O_3$ thin films were synthesized at the reactive gas pressures of $1\times10^{-4}$ to $5\times10^{-4}$ Torr. The Si (100) and glass substrates were held at room temperature. The purity of Al cathode was 99.99%. The $O_2$ gas used in the experiments had the purities of 99.7%.

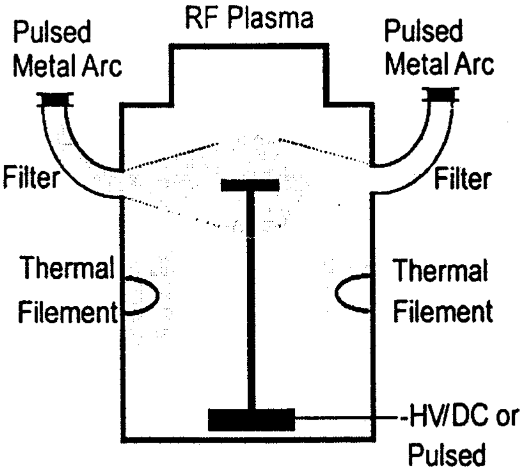

Fig. 1 Schematic of metal plasma immersion ion implantation system developed at the City University if Hong Kong.

### B. Determination of morphology, structure and composition

The morphologies of $Al_2O_3$ thin films were characterized by atomic force microscopy (AFM) and scan electron microscopy (SEM). AFM observation was carried out with autoprobe CP AFM produced by Park Scientific Instruments Ltd. SEM observation was performed on philips XL30 SEM with the accelerating voltage of 10 keV and the resolution of 0.4 nm. A philips CM20 microscopy was used to examined the plane-view morphology and crystal structure of the thin films. Glancing angle incident x-ray diffraction (XRD) on a philips X'Pert diffractometer was also used to study the structure of the thin films. The compositions of thin films were determined by using x-ray photo-spectroscopy (XPS) and Rutherfold backscattering spectrometry (RBS). XPS was carried out on a surface and interface analysis system SIA100. XPS spectra were excited by a Mg $K_\alpha$ x-ray source at the power of 300W and acquired with the energy resolution of 1.0 eV and the step of 0.1 eV.

### C. Characterization of mechanical and optical properties

The microhardness of the thin films was measured on a DMH-2LS microhardness tester, which load can be changed in the range of 0.5 g to 50 g, with Knoop indentor at 2 gf load and 10 s loading duration. The indentation was imaged and measured on a screen. The measurement of adhesion properties was performed on a CSR-01 scratch tester equipped with a 120° diamond indentor by sliding along the surface of the film with the loading speed of 2000 gf/min. The critical load, which resulted in the removal of the film along the sliding track, was taken as a measure of the film adhesion. An ellipsometry was employed to measure the refractive index of thin films and to determinate the thickness of the thin films. The transmittance properties of the thin films were also measured.

## III. RESULTS AND DISCUSSION

### A. Morphology and structure of the thin films

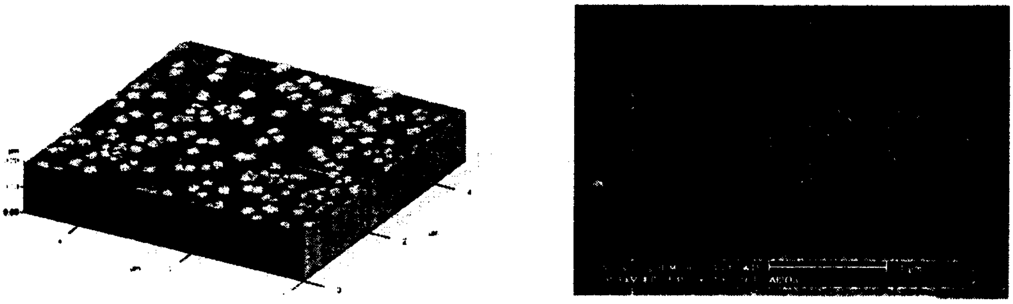

Fig. 2 Morphology of $Al_2O_3$ thin film obtained by (a) AFM (b) SEM.

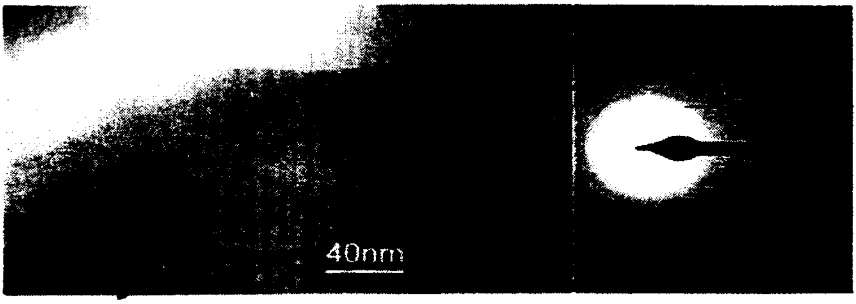

Fig. 3 Micrograph and electron diffraction pattern of $Al_2O_3$ thin film obtained by TEM

The morphologies of $Al_2O_3$ thin films were examined by using SEM and AFM. SEM observation showed that the thin films are very flat and smooth in large scale. AFM and SEM images obtained in small scale, however, show that there are some small islands on the surface of thin film as shown in Fig. 2. These results imply that the thin films grow in the mode of 3-dimensional island growth. The size of growth island is about 0.2 μm. Line scanning AFM shows that these growth islands are sharp. The average value of peak to valley roughness is 11.6 nm and the average value of root mean square roughness is 2.9 nm. The cross-section SEM reveals that the thin films appear to be dense with smooth interface. In fact the cross-section images of the thin films are featureless and could be described as being "glass-like". The cross section SEM also shows the thin films have a good adhesion to substrates.

Figure 3 is a typical TEM micrograph in plane view and associated electron diffraction pattern of the thin films. In the figure we can see that the thin film is a mixture of polycrystalline and amorphous although we cannot determine the crystal structure of polycrystalline in the thin films due to the dispersive diffraction rings. According to the results obtained by other researchers, the polycrystalline might be $\gamma$-$Al_2O_3$ because it easy be formed at lower temperature than $\alpha$-$Al_2O_3$ be formed. GIXD examinations give similar results of TEM observation. The grain size in the thin film is about 2-4 nm.

## B. Composition and binding properties of the thin films

Figure 4 is the RBS and XPS spectra of the thin film obtained at the oxygen pressure of $3\times10^{-4}$ Torr. By fitting to the RBS spectrum, we found the ratio of oxygen to aluminum is 3:2 and the thickness of the thin film is about 180 nm. RBS analysis shows that the ratio of oxygen to aluminum keeps at 3:2 when changing the reactive gas pressure from $1\times10^{-4}$ Torr to $5\times10^{-4}$ Torr. This result means that the composition of the thin films is not sensitive to the reactive gas pressure when the reactive gas pressure higher some certain value.

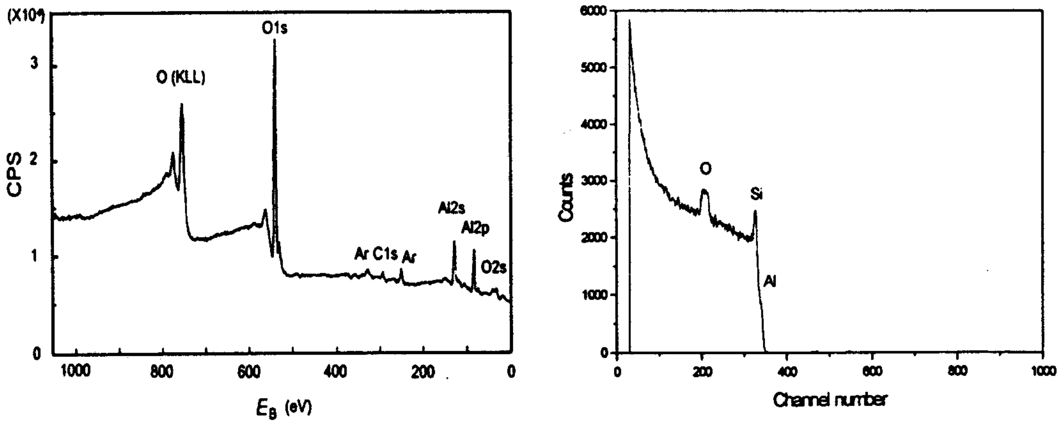

Fig. 4 (a) RBS spectrum and (b) XPS spectrum.

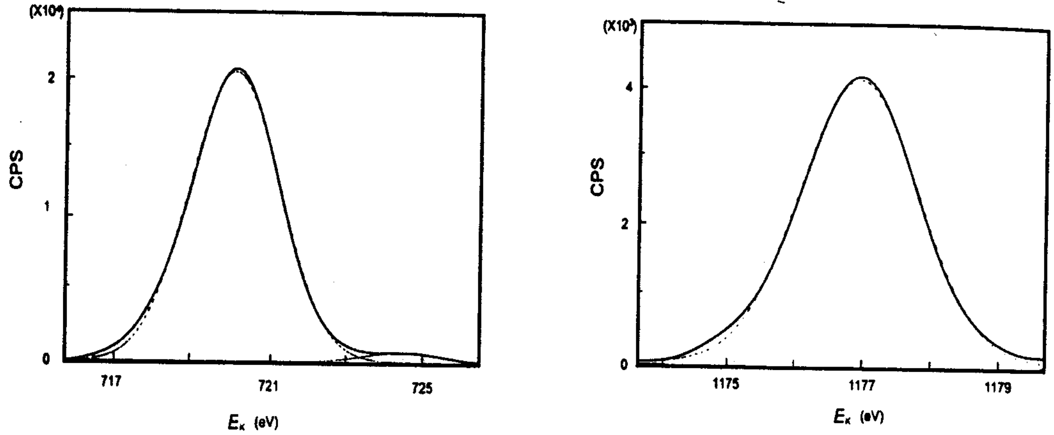

Fig. 5 XPS spectra of (a) $O_{1s}$ and (b) $Al_{2p}$.

In Fig. 4(b) we can see the thin film consists of oxygen and aluminum except of a few carbon in it. XPS quantitative analysis shows that the ratio of oxygen to aluminum is 3:1.9, which is very close to the results obtained by RBS analysis. The binding energies of $O_{1s}$ and $Al_{2p}$ are 531.6 eV and 74.9 eV, respectively, as shown in Fig. 5. They are very close to the results of $Al_2O_3$ (531.5 eV and 74.6 eV for $O_{1s}$ and $Al_{2p}$, respectively) in the handbook of standard XPS spectra given by Perkin Elemer company. We did not find pure $Al_{2p}$ peak in the XPS spectrum, which should appear at 71.5 eV. In other words, the thin film fabricated by filtered pulsed vacuum arc plasma in pure oxygen pressure is a pure $Al_2O_3$ thin film.

### C. Properties of the thin films

The optical properties of the thin film were measured by using transmittance spectroscopy and ellipsometry. All the $Al_2O_3$ thin films fabricated are transparent in the wavelength range of visible light concluded from tramsmittance spectra of the thin films. The refractive index of $Al_2O_3$ thin films determined by using ellipsometry is 1.648, which is in the range of refractive index of $Al_2O_3$ thin films synthesized by other methods, such as RMS, APL, and MBE, *etc.*

Torr.

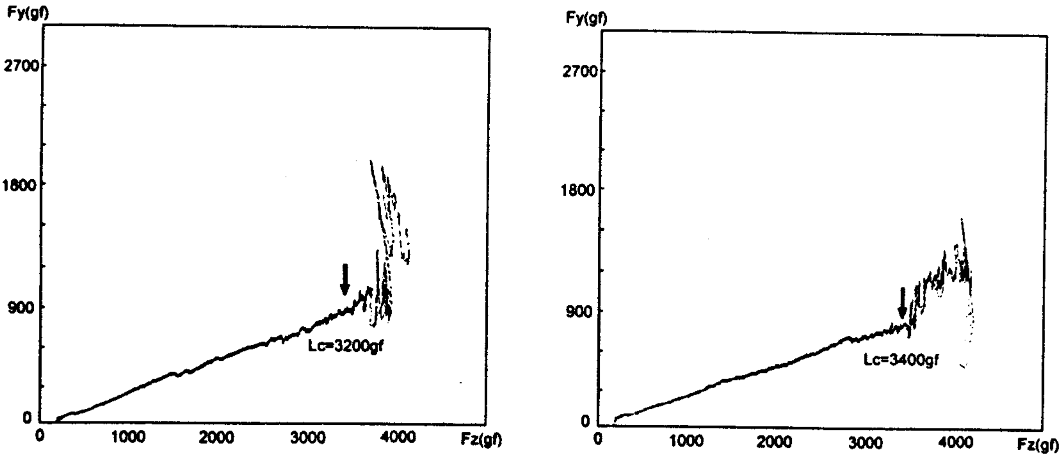

Fig. 6 Scratch test curves of the films fabricated at $O_2$ pressure of (a) $1\times10^{-4}$ and (b) $3\times10^{-4}$

Figure 6 is the results of scratch test of the thin film on glass substrates obtained with various oxygen pressures. We can find the critical load is in the range of 3200 gf to 3400 gf. The results imply that the thin films have good adhesion strength to the substrates, which coinciding with the results of cross section observation by using SEM. The hardness of the thin films detected at the load of 3 g with Knoop's indentor is from 675 to 725 g/mm$^2$. This hardness is lower than that of $Al_2O_3$ films fabricated by other methods, such as IBAD. The reason of low hardness might be the contribution of substrate because the films are too thin.

### D. Discussions

According to the analysis results above, we know that MPIII can be used to synthesize some functional materials with high quality. Due to the high ionization in the vacuum arc and combining the magnetic filter, the metal ion is easy combined with molecules of reactive gas, such as oxygen, in the vacuum camber and the surface of substrate. In fact, the deposition beam is controlled in two folds, the frequency and duration of discharging pulse of vacuum arc. By controlling the deposition beam current of different vacuum arcs, MPIII can also be used to synthesize some multi-component functional materials with an accurate alloy composition. Although the filter is helpful to improve the quality of thin film, the deposition rate is considerably reduced. In other words, MPIII is not suitable to fabricate thick films, such as planar optical waveguide, where a film with thickness of 3-5 μm is needed.

## IV. SUMMARIES

$Al_2O_3$ thin films with stoichiometrical components has been synthesized by using filtered pulsed vacuum arc plasma deposition in the atmosphere of pure oxygen gas.

TEM and GIXD examinations reveal the thin films are the mixture of polycrystalline in nanometer scale and amorphous.

## ACKNOWLEDGMENT

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[1] J.R.Conrad, J.L.Radthe, R.A.Dodd, and F.J.Worzala, **J. Appl. Phys.**, 62 (1987) 4591

[2] K.K.Shih and D.B.Dove, **J. Vac. Sci. Technol., A12** (1994) 321

[3] E.Dorre and H.Hubner, *Aluminum* (Springer, Berlin, 1984)

[4] M.Ritala, H.Saloniemi, M.Leskela, T.Prohaska, G.Friedbacher, and M.Grassebauer, **Thin Solid Films 54** (1996) 286

[5] A.Polman, **J. Appl. Phys., 82** (1997) 1

[6] N.R.Rajopadhye, S.B.Dake, and S.V.Bhoraskar, **Thin Solid Films 142** (1986) 127

[7] B.Lux, C.Colombier, and H.Altena, **Thin Solid Films 138** (1986) 49

[8] P.J.Kelly and R.D.Arnell, **J. Vac. Sci. Technol., A17** (1999) 945

[9] C.J.Kang, J.S.Chun, and W.J.Lee, **Thin Solid Films 189** (1990) 161

[10]K.Sawada, M.Ishida, T.Nakamura, and N.Ohtake, **Appl. Phys. Lett.** 52 (1988) 1672
[11]B.Hirschauer, S.Soderholm, G.Chiaia, and U.O.Karlsson, **Thin Solid Films 305** (1997) 243
[12]Q.Y.Zhang, P.S.Wang, W.J.Zhao, and L.Wang, **Surf. Coatings Technol.**, (2000) in press