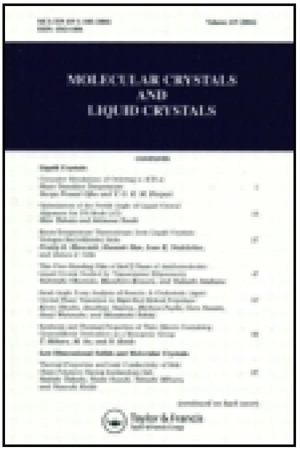
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Self-Assembly of Metal(IV) Alkyldylbisphosphonate Multilayer Films on Gold and Silicon Substrates

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SELF-ASSEMBLY OF METAL(IV) ALKYLDYLBISPHOSPHONATE MULTILAYER FILMS ON GOLD AND SILICON SUBSTRATES

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Abstract Zirconium- and hafnium-alkyldiylbisphosphonate multilayer films are prepared on modified gold and silicon substrates. The substrates are functionalized via 3-(hydroxydimethylsilyl) propanephosphonic acid and mercapto-3-butylphosphonic acid to yield a phosphonic acid surface. Mono- and multilayer films are then prepared by alternatively adsorbing metals such as Zr^{4+} and Hf^{4+}, and α, ϖ-bis(phosphonic acids) from the aqueous solution. The characteristics of multilayer films were characterized by ellipsometry, x-ray reflectometry, AFM and surface plasmon resonance measurement.

INTRODUCTION

Self-assembled mono- and multilayer formed on solid substrates have generated considerable interest recently because of the potential for controlling the molecular architecture and chemical and physical properties of layered assemblies on surfaces.[1-4] We report here a multilayer growth based on the sequential adsorption of components of zirconium, hafnium 1,10-decanebisphosphonate(Zr-, Hf-DBP). Metal-phosphonates[5-7] are an ideal choice for this kind of growth because as bulk phases their morphology resembles that of Langmuir-Blodgett multilayers.[7] To evaluate such properties as degree of order, number of defects, film thickness and reproducibility of layer formation, we have used ellipsometry and x-ray reflectivity(XRR). Most of all, X-rays has proved to be a powerful, marvelous nondestructive technique for the study of the structure and morphology of thin films and interfaces.[8-9] X-ray scattering is capable of yielding quantitative global statistical information about surface and buried interfaces over an enormous range of length scales(angstroms to microns).

EXPERIMENTAL

Preparation of Zirconium, Hafnium -DBP multilayer

1 mM methanol solution of 3-(hydroxydimethylsilyl) propanephosphonic acid as anchoring agent was used, then Zr-,Hf-functionalized Si(100) wafer was placed alternately into aqueous solutions of 1 mM DBPA and 20 mM Zr,$HfOCl_2$-$8H_2O$. Between immersions in the alternation solutions, the wafer was rinsed in flowing D.I. water for 5 min and dried under purging N_2. Figure 1 shows a scheme for formation of Hf-DBP multilayers.

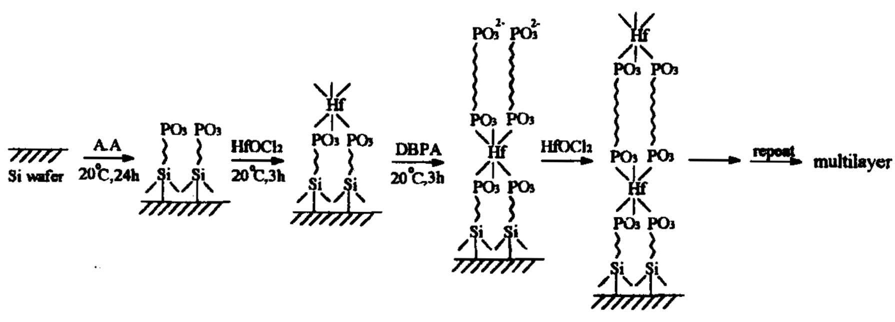

FIGURE 1 Synthetic scheme for formation of Hf-DBP multilayers.

X-ray reflectivity

X-ray reflection data was obtained in PLS(Pohang Light Source). X-ray reflectivity and diffuse scattering measurements were performed at the absorption edge of Co monochromated by Si(111) double crystal with a fixed-exit beam geometry. The monochromator provides photons of energy between 4-12KeV. Figure 2 shows a schematic view of experimental setup for x-ray reflectivity.

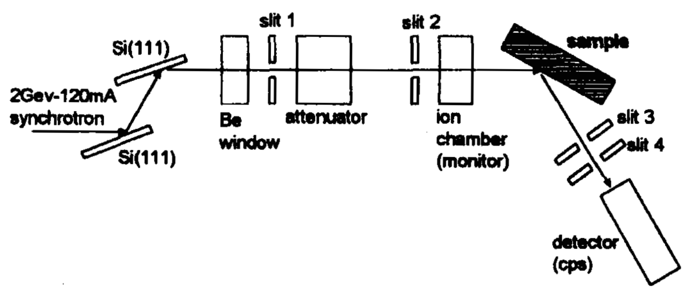

FIGURE 2 Schematic view of experimental setup for x-ray reflectivity

RESULTS AND DISSCUSION

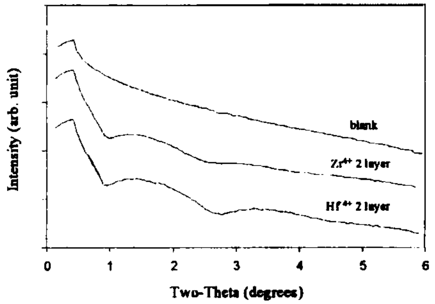

FIGURE 3 X-ray reflectivity of Zr-, Hf-DBP two layer film(Calculated thickness is 23 Å/layer for each case of Zr-,Hf-DBP).

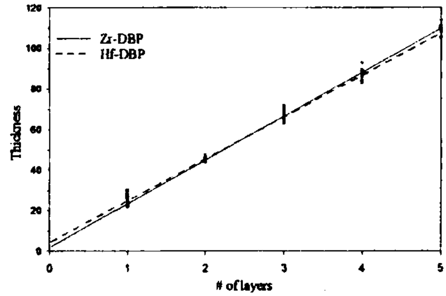

FIGURE 4 Ellipsometry results of Zr-, Hf-DBP multilayer(thickness of anchoring layer is 6 Å, and layer thickness of Zr-,Hf-DBP is 20 Å, refractive index of multilayer film is 1.53)

X-ray reflectivity data of multilayer Zr-, Hf-DBP films show peaks, or fringes, at low angles(0.9-4°, 2θ). Representative data for two layer films are shown in Figure 3. In general, as the thickness of the film increases, the number of observed fringes increases and they move to lower angle.[4] Such fringes are attributed to interference between reflection of x-rays from the front and the back of the film. The calculated film thickness of Zr-, Hf-DBP multilayer films is 22-23 Å/layer. The thickness of Zr-DBP was also measured by using *in-situ* surface plasmon resonance(SPR) measurement.[10] Our SPR data could be best described by a layer thickess of 2 nm for Zr-DBP assuming the refractive index of 1.50 on the top of anchoring agent on either gold or silicon surfaces. The calculated thickness derived from x-ray data is similar to the value derived from ellipsometry (Figure 4) and SPR which can estimate the thickness of anchoring agent and Zr-DBP on gold surface. The SPR data give us Zr-DBP layer thickness by measuring reflectivity on angle.

One proposed model could be domains within each layer that correspond to regions having a particular alkyl chain density, tilt angle and orientation. These domains are presently influenced by lateral metal density on the modified substrate surfaces. Such domains bring out the different thickness and the variations in total film thickness as well as the lack of a well-defined Bragg reflection corresponding to the individual layer spacing. Furthermore, domain boundaries also could be disordered and give the low vertical and lateral ordering. Interface of the each layer could not be well ordered as expected. Roughness of interface, which affects the low degree of lateral order of each interface, should be a little large. AFM results show the initially well-ordered monolayer structure on gold, but as the number of layers increases, the less ordered layer structure was observed. This result supports the low degree of lateral order of layer structure as the number of layers increases. Therefore, once we highly-ordered multilayer structures, we can reveal the structural information in detail by using XRR, SPR and AFM measurements.

CONCLUSION

Zr-,Hf-DBP multilayers were prepared on gold and silicon surfaces. And the characteristics of these films are studied via XRR, surface plasmon resonance, AFM and ellipsometry measurements. The average thickness of the film derived by XRR is about 22-23 Å, and the values derived from ellipsometry and surface plasmon resonance is about 18-20 Å. This difference is presumably dependent upon the lateral density of surface binding sites .

ACKNOWLEDGMENT

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