

# keV SURFACE MODIFICATION AND THIN FILM GROWTH

Seok-Keun Koh, Won-Kook Choi, Young-Soo Youn, Seok-Kyun Song, Jun-Sik Cho, Ki-Hwan Kim and Hyung-Jin Jung  
Division of Ceramics, Korea Institute of Science and Technology  
P. O. Box 131, CHEONGRYANG, SEOUL 136-791, KOREA,

## ABSTRACT

keV ion beam irradiation for surface modification and thin film growth have been discussed. keV ion beam irradiation in reactive gas environment has been developed for improving wettability of polymer, and for enhancing adhesion to metal film, and advantages of the method have been reviewed. An epitaxial Cu film on Si(100) substrate has been grown by ionized cluster beam and changes of crystallinity and surface roughness have been discussed. Stoichiometric SnO<sub>2</sub> films on Si(100) and glass have been grown by a hybrid ion beam Deposition( 2 metal ion sources + 1 gas ion source), and nonstoichiometric SnO<sub>2</sub> films are controlled by various deposition conditions in the HIB. Surface modification for polymer by keV ion irradiation have been developed. Wetting angle of water to PC has been changed from 68 degree to 49 degree with Ar<sup>+</sup> irradiation and to 8 degree with Ar<sup>+</sup> irradiation and the oxygen environment. Change of surface phenomena in a keV ion beam and characteristics of the grown films are suggested.

## 1. INTRODUCTION

From macromechanic to micromechanics, and from simple device to complicated ULSI, surface modification of materials, high quality epitaxial metal films, and formation of stoichiometric or nonstoichiometric ceramic thin film have been much interested in fabricating intergrated circuits, creating new functional device on surface, protecting substance in severe environments, and constructing complicated quality intergrated sensor. Many studies(1-7) have been carried out in order to control thickness, surface roughness, crystallinity, and nonstoichiometry of materials for creating high quality and high functional devices.

In the case of surface modification or thin film formation, it has been considered to solve many difficulties in the conventional surface modification or in the thin film formation by adjusting depositing atom's or molecule's energy themselves. The arrangement of energetic atoms or rearrangement by energetic ion assistance with controlling particle's energy can reduce the substrate temperature, create sharp interface, and grow preferred orientation in the formation of high quality thin films. These modification methods, such as ion assisted deposition, physically ionized beam, etc., can also solve the cleaning of chemisorbed or physisorbed impurities by physical sputtering in which the action of energetic bombardment should increase the adhesion between growing thin film and substrate. The irradiation of energetic particles onto the substrate has assisted to form the large size nuclei which are important factors in the film formation, and have changed properties of thin films such as crystallinity, nonstoichiometry, surface morphology, etc., and have modified surface properties of metal, ceramics and polymers by controlling particles energy.

In the article, we reviewed a surface modification of polymer by keV ion irradiation, a nonstoichiometric SnO<sub>2-x</sub> thin film growth by hybrid ion beam, and an epitaxial Cu thin film growth on Si(100) surface by ionized cluster beam with various acceleration voltages and ionization potentials, and have tried to suggest advantages and prospectives of the films and modification.

## 2. EXPERIMENT

One UHV metal ion beam deposition and 2 hybrid ion beam deposition systems are designed and constructed for high quality metal film formation, ceramics films, ion beam sputter deposition, surface cleaning, and surface modification of materials in the laboratory. The UHV metal ion beam system consists of one metal ion beam source in a main growth chamber, and a sample load lock chamber. Base vacuum pressure is 10<sup>-9</sup> torr, and the working pressure in the deposition and in the substrate cleaning process are 2-3x 10<sup>-8</sup> torr. In order to confirm characteristics of metal ion source, mainly considering the effect of residual gas and ionization efficiency, the results of this article are obtained in the 10<sup>-7</sup>- 10<sup>-6</sup> torr range. The hybrid ion beam systems which have base pressure of 10<sup>-6</sup> torr compose of 2 metal ion sources and one gas ion source are worked for SnO<sub>2-x</sub> films formation and for surface modification of polymers. The

characteristics of metal ion source and of metal ion source in reactive gas environments have been investigated for metal film formation and ceramic film formation.

### 3. RESULTS AND DISCUSSION

Beam uniformity of metal ion source is investigated with changing distance between faraday cup and the source. Cu films were deposited on Si (100) substrate by ionized cluster beam in a pressure of  $10^{-6}$  torr. Ion beam current densities were measured with and without Cu evaporation, respectively, in order to evaluate an effect of residual gas on the Cu deposition process. The ion beam current density measured without Cu evaporation, which is mainly due to ionized residual gas, was linearly increased with acceleration voltage, and the dependence of the ion beam current density on vacuum pressure was significantly decreased with  $10^{-5}$ - $10^{-7}$  torr. Total ion beam current density measured during Cu deposition, effects of ionized Cu particles and residual gas, was increased with acceleration voltage, and the magnitude of the total ion beam current density is nearly the same as the ion beam current density due to ionized residual gas. It has been found that not only metal ion beam but also residual gas ion beam play important role in the film formation.(2)

Many attempts have been carried out to modify the surface and to grow high quality thin films through the heated substrate or the conventional chemical reaction which be the interface of the energy transfer for the decomposition of organometallic reagents in chemical vapor deposition, which be the surface layer of the growing atoms in the molecular beam epitaxy, and which be thermodynamic wet chemical reaction with creating interface chemical reaction, diffusing metal to the substrate, and contaminating organic elements( carbon, oxygen, nitrogen, etc.) in the metallization or the compound formation process. Epitaxial growths with closely relating the substrate structure have been controlled by substrate temperature, in which there are some limitations of choosing the substrate with relating the lattice misfit. The epitaxial growth or crystallization mechanism have much closely related to size of atoms and structure which are composed of substrate because the growing energy transfers from the substrate with remaining difficulties of chemically and physically absorbed impurity cleaning process. Because of the substrate's dependence, the step coverage of metal films on the trenched substrate, and the epitaxial growth have difficulties in conventional physical vapor deposition and chemical vapor deposition.

Epitaxial Cu thin film on Si(100) substrate has been grown on the room temperature substrate in the UHV metal ion beam system(Figure 1), and has high thermal stability where the films are annealed at 400 °C for 30 min.(Figure 2).

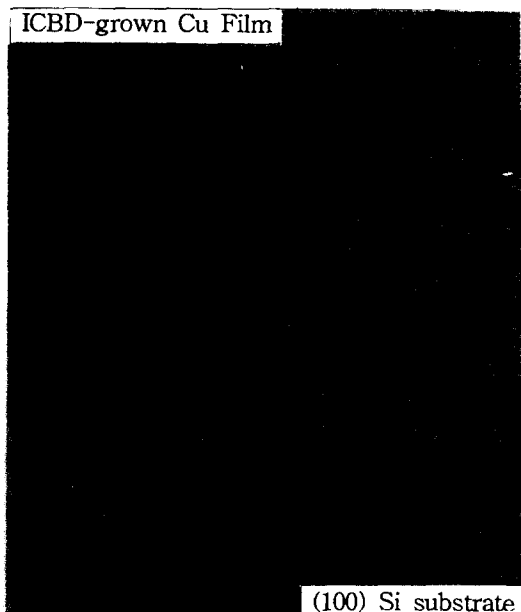


Figure 1. High resolution TEM of Cu/Si(100) deposited at 3keV acceleration voltage. The image shows perfect growth of Cu(111) on room temp. Si(100)substrate.

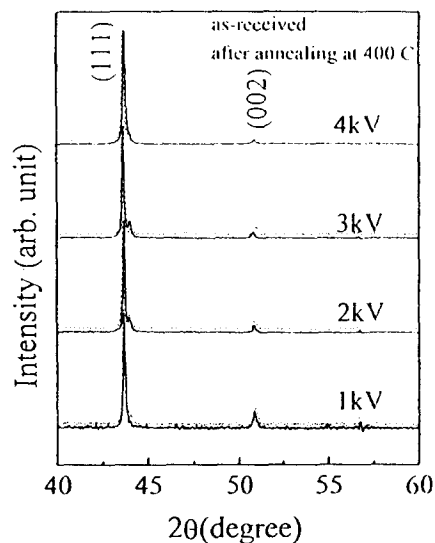


Figure 2. X-ray diffraction of Cu thin film which were grown on room temp. Si(100)substrate with various acceleration voltages.

The dotted lines represent XRD after annealed at 400°C for 30 min.

The growth condition of the films can be adjusted by acceleration potential from 0 to 4 kV at 400 V ionization potential

The hydrophilic group formation mechanism is explained by a two-step-reaction model, in which the first step is a creation of unstable chemical group in the polymer matrix by energetic Ar<sup>+</sup> ion irradiation and the second is a formation of hydrophilic group between the unstable chemical group and oxygen gas(7). Moreover a keV energy generation with large size beam can be produced by simple ion beam sources which have been mainly applied to ion beam sputtering, surface cleaning, reactive ion etching, etc., and does not require complicated expensive facilities(6).

#### 4. CONCLUSIONS

The Cu thin film and the SnO<sub>2-x</sub> thin film growth by ion beam techniques, and keV ion irradiation for polymer surface modification have been discussed. Degree of crystallinity  $R=I(111)/I(100)$  was varied from 6 to 37 and Root Mean Square(Rms) of surface roughness was changed from 14 Å to 137 Å in the grown Cu films when acceleration voltage(Va) and ionization potential(Ip) are adjusted. Nonstoichiometric tin oxides have been grown by hybrid ion beam techniques. Contact angle of water to PC has been reduced from 68 degree to 49 degree with Ar<sup>+</sup> irradiation, and to 8 degree with Ar<sup>+</sup> irradiation in various vacuum pressure adjusted by oxygen gas flow rate. Effects of Ar<sup>+</sup> ion were explained in a view of formation of hydrophilic group due to a reaction between irradiated polymer chain by energetic ion irradiation and blowed oxygen, and enhanced adhesion between Aluminum and PMMA was explained by formation of electron acceptor group in polymer and electron donor in metal, and interfacial chemical reaction between irradiated polymer surface and deposited metal.

#### References

1. S. K. Koh, H. J. Jung, and K. H. Kim, Applied for Patents(K-1137) to U.S.A., Japan, Korea., Oct. (1994).
2. S. K. Koh, Z. Jin, J. Y. Lee, H.J. Jung, K. H. Kim, and D. J. Choi, *J. Vac. Sci. & Technol A*. Printed on Aug. 1995.
3. S. K. Koh, H. J. Jung, J. Y. Lee, and Z. Jin, Applied for Patents to U.S.A. and Korea, Japan, Oct. 1994.
4. S. K. Koh, H. J. Jung, W. K. Choi, S. K. Song, D. S. Choi, and J. S. Jeon, Applied for Patents to U.S.A. Japan, and Korea, April, 1995.
5. S. K. Koh, H. J. Jung, and S. N. Han, Applied for Patents(9194) to U.S.A., and Korea, Dec. 1994.
6. S. K. Koh, H. J. Jung, W. K. Choi, S. K. Song, J. S. Cho, Y. S. Yoon, and C. K. Choi, Applied for Patents to U.S.A., Japan, and Korea, June, 1995.
7. S. K. Koh, W. K. Choi, S. K. Song, H. J. Jung, and S. N. Han, *J. Mat. Res.* Printed on Aug. 1995.