LBNL-51568

Submitted to
*The International Conference on Metallurgical Coatings and Thin Films*
(ICMCTF 2003)

A reviewed version of the full manuscript may be accepted in either
"Surface and Coatings Technology" or "Thin Solid Films"

# Effect of underlayer on coalescence of silver islands grown by filtered cathodic arc deposition

**Eungsun Byon[a)], and André Anders[b)]**

[a)]Korea Institute of Machinery and Materials, 66 Sangnam-Dong,
Changwon, 641-010, Korea
[b)]Lawrence Berkeley National Laboratory, University of California,
1 Cyclotron Road, Berkeley, California 94720-8223

Full version is due March 1, 2003.

Corresponding Author:
André Anders
Lawrence Berkeley National Laboratory
1 Cyclotron Road, MS 53-004
Berkeley, CA 94720, USA
Tel. + (510) 486-6745
Fax + (510) 486-4374
e-mail aanders@lbl.gov

This work was supported by the Laboratory Technology Research Program (SC-32), within the Office of Science, and by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Building Technology, U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Eungsun Byon was supported by the post-doctoral fellowship program of the Korean Science and Engineering Foundation (KOSEF).

# Effect of underlayer on coalescence of silver islands grown by filtered cathodic arc deposition

Eungsun Byon, André Anders*

Korea Institute of Machinery and Materials, 66 Sangnam-Dong,

Changwon, 641-010, Korea

* Lawrence Berkeley National Laboratory, University of California,

1 Cyclotron Road, Berkeley, California 94720-8223

**Abstract**

Ultrathin silver films that are not continuous show relatively high absorption in the visible and low reflection in the infrared. For low-emissivity application on window glass, coalescence of silver islands is crucial for obtaining the desired optical properties of the coating, namely high transparence in the visible and high reflectivity in the infrared. It is well known that the energy of ions arriving at the substrate and the type of underlayer affect nucleation and growth of silver islands. There are a number of studies on nucleation and growth, but little is known about coalescence of silver islands synthesized by more energetic condensation, e.g. filtered cathodic vacuum arc (FCVA). In this work, the effect of underlayer on nucleation and growth of silver films deposited by FCVA was investigated by transmission electron microscopy (TEM) and atomic force microscopy (AFM). The results are compared with data obtained by magnetron sputtering.

From the results, plane and titanium-oxide-coated glass requires more material to achieve the same value of resistance than for the zinc oxide coated glass. It is related with the energy of interaction between the surface and the silver atom. Silver films made by cathodic arc deposition show an earlier

onset of island coalescence and formation of short links. It was found that silver islands in energetic deposition exhibit a reduced aspect ratio when compared to evaporation and sputtering. Nb underlayer affects nucleation and growth of coalescence of silver only in the case of few monolayer of Nb was introduced.

## 1. Introduction

Spectrally selective, transparent coatings are of great interest for energy-efficient window coatings. In cold climates, low-emittance (low-E) coatings with high solar transmittance ($0.3 < \lambda < 3$ μm) and high thermal infrared (IR) reflectance ($3 < \lambda < 100$ μm) are required, while in warm climates solar control coatings of high luminous transmittance ($0.4 < \lambda < 0.7$ μm) and high near-infrared reflectance ($0.7 < \lambda < 3$ μm) are beneficial. Both types of coatings can be obtained by embedding a thin metal film between anti-reflecting dielectric layers.[1)] It is known that low-emittance and high infrared reflectivity is directly related to the sheet resistance of the metal layer.[2)] Silver is the metal of choice because of its high conductivity and color-neutral transmission in the visible range of the spectrum. To maximize transmission in the visible and reflectance in the IR, it is desirable to produce a very thin silver film that is as conducting as possible.

It is known that silver on oxides grows in the Volmer-Weber mode, i.e. silver islands are formed before a continuous film is obtained.[3)] Ultrathin silver films consisting of islands show relatively high absorption in the visible and low IR reflection. Coalescence of silver islands is therefore crucial for obtaining the desired optical properties of the coating. Commercially, silver films of about 12 nm thickness are produced for low-E application on a very large scale by magnetron sputtering on oxide-coated flat glass.[2)] There exists a number of studies on nucleation and growth of metals on oxides, e.g.[1,4-7)]. Whilst nucleation, island growth, and coalescence has been investigated for evaporated[8)] and sputtered[9)] silver films, little is known about silver films synthesized by energetic condensation. In

energetic condensation,[10,11] film-forming atoms or ions arrive at the substrate surface with hyperthermal energies, typically in the range of 10-100 eV, leading to subplantation and nano-scale thermal spikes around the arriving particle's impact location.[12] Filtered cathodic arc vacuum (FCVA) deposition is a prominent example for energetic condensation. Thin gold films deposited by FCVA deposition have a lower roughness than evaporated and sputtered films.[13] In this work we focus on coalescence of silver on oxide surfaces produced by FCVA deposition. The effect of Nb underlayer on nucleation and growth of silver films was also investigated.

## 2. Experimental

The experimental setup is shown in Fig. 1. A miniature pulsed cathodic arc plasma source[14] with a cylindrical silver cathode of 6.25 mm diameter was operated with a 10-stage pulse-forming network.[15] The arc current pulses had a rectangular shape with 1.2 kA amplitude and 620 μs pulse width, with a pulse repetition rate of 1.6 pps. The plasma source injected streaming silver plasma into a 90° magnetic macroparticle filter.[16] This filter was an open solenoid used to remove microscopic debris ("macroparticles") produced at cathode spots. Neutral silver vapor, if present in the flow, is also removed by the filter, and thus fully ionized silver plasma arrived at the substrates, which were located 200 mm from the filter exit. The silver plasma streaming velocity was 11,100 m/s, corresponding to an average kinetic energy of 70 eV, and the mean ion charge state was 2.1.[17] The chamber was cryogenically pumped to a base pressure of about $10^{-4}$ Pa; no process gas was needed or used.

Uncoated glass standard microscope slides, magnetron-sputtered zinc-oxide-coated glass, and titanium-oxide-coated glass were used as substrates. The samples were mounted on a water-cooled substrate holder. The substrate temperature was generally near room temperature although the surface is subject to heating by the deposition process. It is known[18] that the $TiO_2$ layer is amorphous while the ZnO layer is polycrystalline with {0001} orientation.

Coalescence of silver islands can be detected by measuring the onset of electronic conduction. The film resistance was measured *in-situ* during deposition. For that purpose, two silver contact pads, approximately 1 μm thick, were deposited on the 25 mm wide samples prior to the experiments. The contact pads were 25 mm apart and thus an area of 25 mm x 25 mm was defined. The resistance between the contact pads was measured using a Keithley 177 precision multimeter, directly giving the sheet resistance in Ohms per square. A possible effect of the measuring current was considered as discussed below.

The deposition rate was calibrated ex-situ by measuring step heights of a relatively thick film (100 nm) using a Dektak profilometer. The nominal thickness of ultrathin films can easily be determined by counting arc pulses under the assumption that the deposited film thickness is directly proportional to the number of arc pulses. One needs to stress that film thickness determined this way needs to be understood as nominal, especially at the beginning of the deposition process when the "film" actually consists of islands. The deposition rate was determined to be 0.023 nm/pulse, corresponding to about 1/10 of a monolayer per pulse, an instantaneous rate of 37 nm/s and an average rate of 0.037 nm/s.

For comparison, ultrathin silver films have also been deposited in the same process chamber by DC-magnetron sputtering. The same kinds of substrates were placed 100 mm in front of a 3" sputter gun with a silver target. The argon pressure during sputtering was 66 mPa. The sputter power was 40 W with a target potential of –390 V, leading to a deposition rate of 0.75 nm/s.

To investigate the effect of underlayer on nucleation and growth of silver films, Nb layer with different thickness was deposited prior to silver deposition using pulsed cathodic arc plasma source with Nb cathode. All the deposition conditions were same as the silver deposition expect number of arc pulses. The thickness of Nb layer was controlled to 0.1 or 0.2 nm by thickness calibration as mentioned above.

The nucleation and growth of silver films deposited by FCVA and sputtering were examined by transmission electron microscopy (Jeol, JEM-200FXII) and atomic force microscopy (Digital Instruments, Nanoscope IIIa ). For TEM observation, silver films were deposited on back-etched Si with 50 nm thick LPCVD amorphous $Si_3N_4$ electron transparent membranes.

## 3. Results

The in-situ sheet resistance of the film decreased as expected with increasing amount of material deposited. Fig. 2 shows the resistance as a function of the number of arc pulses for Ag deposited on plane glass, zinc-oxide-coated glass, and titanium-oxide-coated glass. The sheet resistance as a function of nominal thickness indicate three regions: (i) the region of individually dispersed clusters and islands, (ii) a transition region where short-link conduction starts, and (iii) a region where a continuous film is formed, gradually approaching bulk resistivity when the film thickness much exceeds the electron mean free path (Drude model). From the Fig. 2, uncoated and titanium-oxide-coated glass requires more material to achieve the same value of resistance than for the zinc oxide coated glass. It is related with the energy of interaction between the surface and the film. If the interaction energy between the adatoms and the atoms on the surface of the substrate is lower than the energy between the adatoms themselves, then the film will grow as discrete islands centered on initial nucleation sites.[19)] It seems that the interaction between the zinc-oxide surface and the silver atoms is more strong that those of titanium-oxide-coated glass and uncoated glass. For this reason zinc-oxide-coatings are often used as substrate for low-emittance optical coatings obtained by sputtering.

The energetics of the deposition process and the substrate material and temperature are known to affect the transition region and formation of a continuous film. This is illustrated by the difference between the curves for cathodic arc and magnetron deposited silver on glass and ZnO as shown in Fig. 3. Nucleation and growth in energetic deposition is different because film-forming ions arrive with high

kinetic energy. Cathodic arc Ag ions have an average kinetic energy of 70 eV, as compared to the 1-3 eV in sputter deposition. Consequently, Silver films made by cathodic arc deposition show an earlier onset of island coalescence and formation of short links. This indicates that silver islands in energetic deposition exhibit a reduced aspect ratio when compared to evaporation and sputtering. To confirm this, morphologies of cathodic arc deposited and sputter deposited silver islands were observed by TEM. Fig. 4 shows TEM micrographs of the filtered arc deposited and sputtered silver films with 10 ohm of sheet resistance at 8 and 16 nm in thickness, respectively. It can be seen that small and fine islands were formed in arc deposited silver layer, comparing with sputtered one, which shows coarse and irregular in size of islands.

Fig. 5 shows sheet resistance of filtered arc deposited silver films on titanium-oxide-coated glass and Nb underlayer with different thickness. Sheet resistance curves of silver layer on Nb underlayer show faster transition and onset of electronic conduction that is than that of silver films with no Nb underlayer. When the Nb thickness is 0.1 nm, it was measured the onset of electronic conduction at about 7 nm. With increasing the thickness of Nb underlayer to 0.2 nm, however, less improvement of electronic conduction could be seen. It indicates that only few monolayer of Nb accelerates the nucleation and growth of silver islands. Fig. 6 shows the islands morphologies of silver formed on titanium-oxide-coated glass and Nb underlayer with different thickness. It can be seen that according as introduce Nb underlayer with 0.1 nm in thickness between silver and substrate, fine and dense islands of silver was formed. It indicates that silver islands on 0.1 nm of Nb layer exhibit a reduced aspect ratio as shown in Table 1.On the contrary, size and morphology of silver islands were larger and rough in the case of 0.2 nm of Nb underlayer.

## 4. Conclusion

Plane and titanium-oxide-coated glass requires more material to achieve the same value of resistance than for the zinc oxide coated glass. It is related with the energy of interaction between the surface and the silver atom. The energetic differences between filtered cathodic arc deposition and magnetron sputtering lead to distinct film properties. Silver films made by cathodic arc deposition show an earlier onset of island coalescence and formation of short links. It was found that silver islands in energetic deposition exhibit a reduced aspect ratio when compared to evaporation and sputtering.

Nb underlayer affects nucleation and growth of coalescence of silver only in the case of few monolayer of Nb was introduced.

## References


[1] G. B. Smith, G. A. Niklasson, J. S. E. M. Svensson, and C. G. Granqvist, J. Appl. Phys. **59,** 571 (1986).

[2] H. J. Gläser, *Large Area Glass Coating* (Von Ardenne Anlagentechnik GmbH, Dresden, Germany, 2000).

[3] R. Lazzari and J. Jupille, Surface Sci. **482-485,** 823 (2001).

[4] S. Xu and B. L. Evans, J. Mat. Sci. **27,** 3108 (1992).

[5] A. I. Maaroof and B. L. Evans, J. Appl. Phys. **76,** 1047 (1994).

[6] M. Avrekh, O. R. Monteiro, and I. G. Brown, Appl. Surf. Sci. **158,** 217 (2000).

[7] E. V. Barnat, D. Nagakura, P.-I. Wang, and T.-M. Lu, J. Appl. Phys. **91,** 1667 (2002).

[8] B. Gergen, H. Nienhaus, W. H. Weinberg, and E. M. McFarland, J. Vac. Sci. Technol. B **18,** 2401 (2000).

[9] M. Arbab, Thin Solid Films **381,** 15 (2001).

[10] O. R. Monteiro, Annual Rev. Mat. Sci. **31,** 111 (2001).

[11] J. S. Colligon, J. Vac. Sci. Technol. A **13,** 1649 (1995).

[12] A. Anders, Appl. Phys. Lett. **80,** 1100 (2002).

[13] A. Bendavid, P. J. Martin, and L. Wieczorek, Thin Solid Films **354,** 169 (1999).

[14] R. A. MacGill, M. R. Dickinson, A. Anders, O. R. Monteiro, and I. G. Brown, Rev. Sci. Instrum. **69,** 801 (1998).

[15] A. Anders, R. A. MacGill, and T. A. McVeigh, Rev. Sci. Instrum. **70,** 4532 (1999).

[16] A. Anders, Surf. Coat. Technol. **120-121,** 319 (1999).

[17] A. Anders and G. Y. Yushkov, J. Appl. Phys. **91,** 4824 (2002).

[18] R. Dannenberg, D. Glenn, and E. Stach, Tech. Conf. of Society of Vacuum Coaters, Philadelphia, 2001, pp. 218-224.

[19] Sainty, W., Protection of optical surface by this films. PhD Thesis, University of Sydney, 1994.

Table 1. Roughness of silver islands formed on titanium-oxide-coated glass and Nb underlayer with different thickness.

| | $R_a$ (nm) | $R_q$ (nm) | $R_{max}$ (nm) |
|---|---|---|---|
| Ag/$TiO_2$ | 2.2 | 2.9 | 27.6 |
| Ag/Nb(0.1nm)/ $TiO_2$ | 0.65 | 0.81 | 5.85 |
| Ag/Nb(0.2nm)/ $TiO_2$ | 2.33 | 3.2 | 30.34 |

**Figure Captions**

FIG. 1 Experimental setup for filtered cathodic vacuum (FCVA) arc deposition of thin metal films.

FIG. 2 Sheet resistance of filtered arc deposited silver films on different substrates, which is expressed as nominal film thickness, measured immediately after completion of deposition.

FIG. 3 Sheet resistance of sputtered and filtered arc deposited silver films as a function of incident silver dose, which is expressed as nominal film thickness, measured immediately after completion of deposition.

FIG. 4 TEM micrographs of a) filtered arc deposited and b) sputtered silver films with 10 ohm of sheet resistance at 8 and 16 nm thickness, respectively.

FIG. 5 Sheet resistance of filtered arc deposited silver films on $TiO_2$ substrate and Nb underlayer with different thickness.

FIG. 6 AFM images of filtered arc deposited silver films on $TiO_2$ substrate and Nb underlayer with different thickness; a) no underlayer, b) 0.1 nm of Nb underlayer and c) 0.2 nm of Nb underlayer.

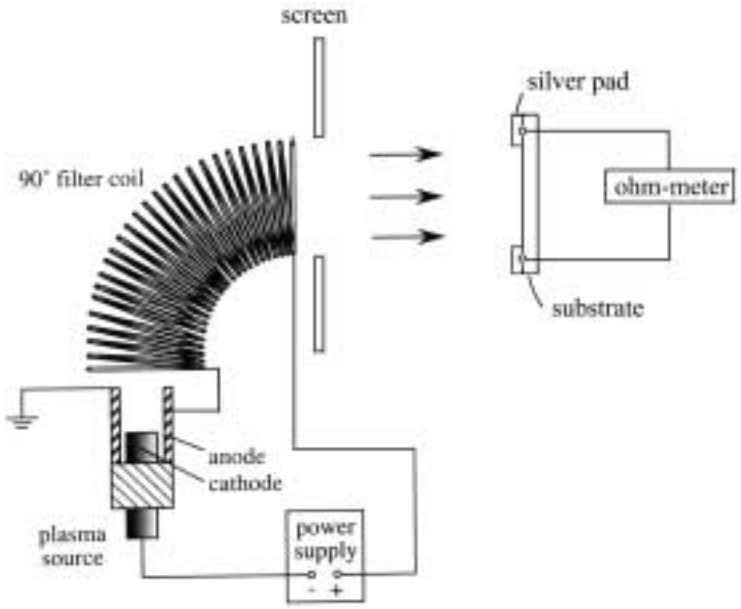


Fig. 1, B2-7

(Byon et. al.)

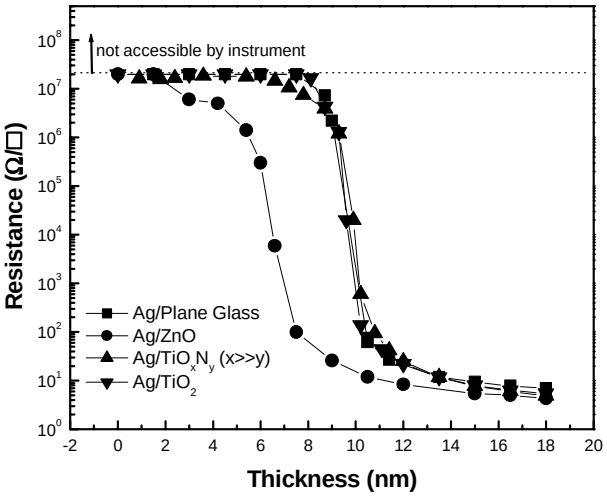


Fig. 2, B2-7

(Byon et. al.)

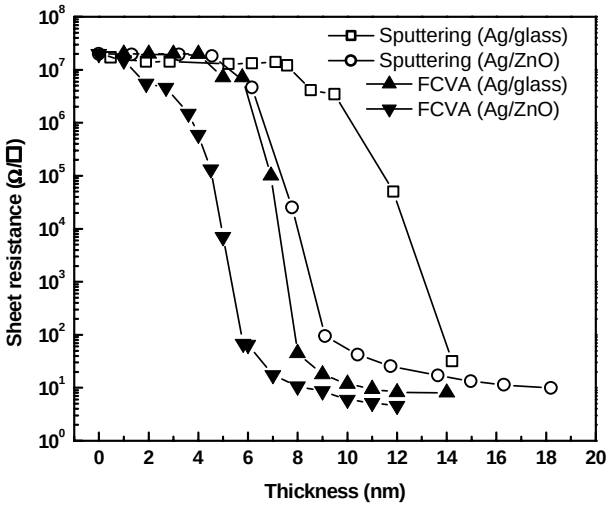


Fig. 3, B2-7

(Byon et. al.)

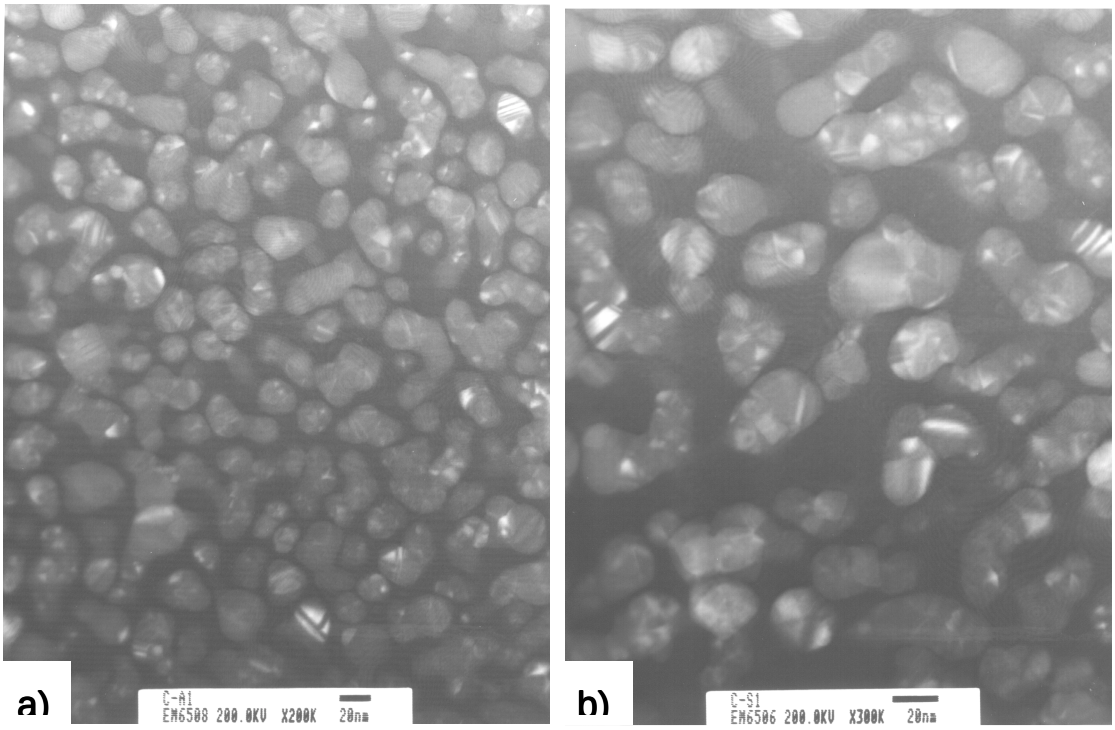


Fig. 4, B2-7

(Byon et. al.)

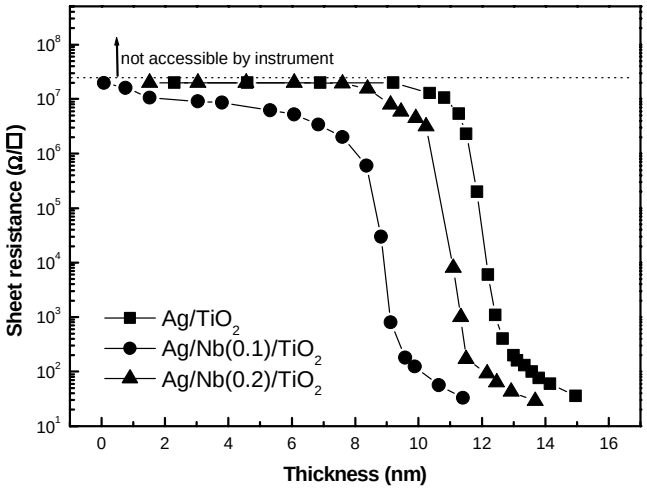


Fig. 5, B2-7

(Byon et. al.)

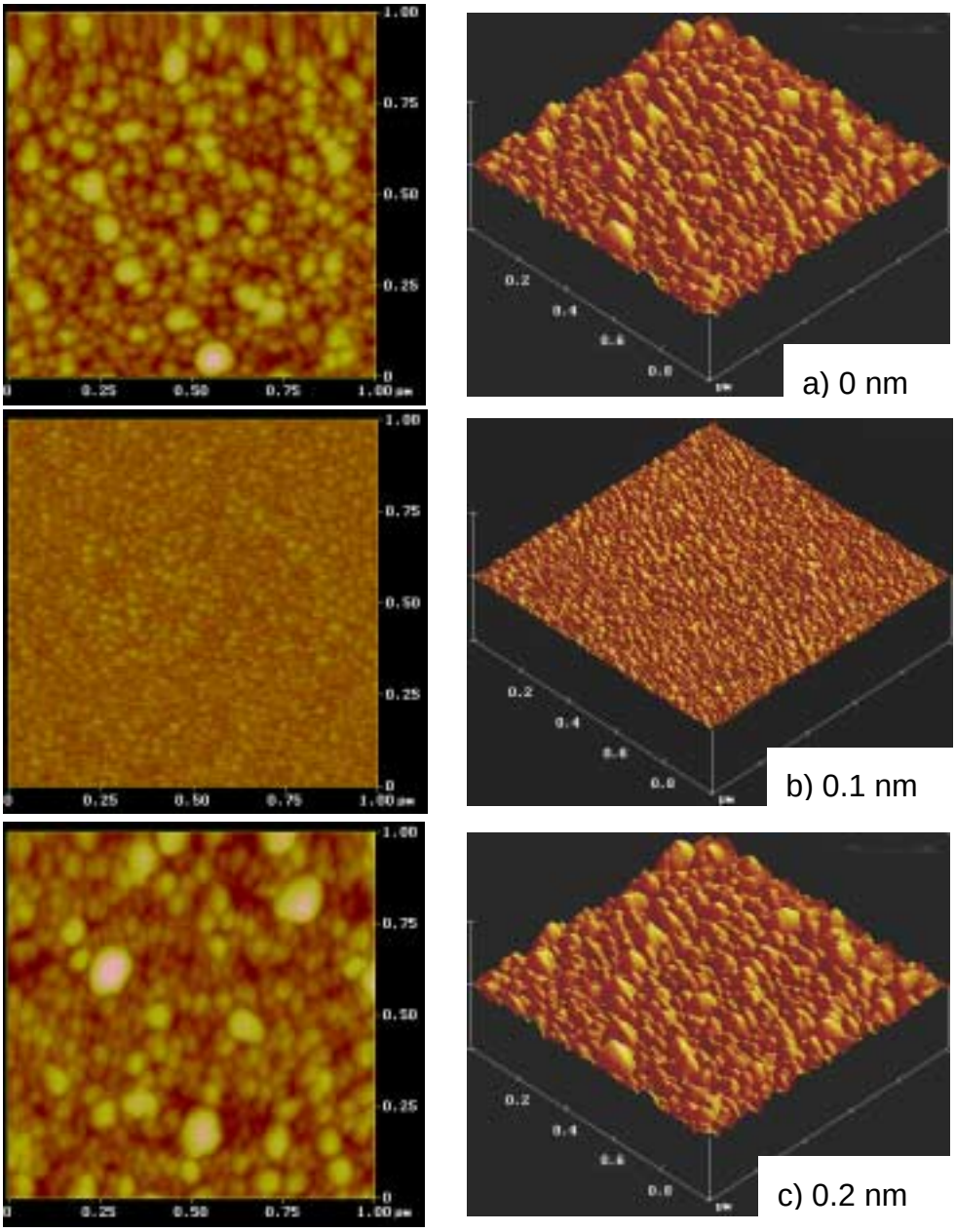


Fig. 6, B2-7

(Byon et. al.)