

Supporting Information

Texture orientation of silver thin films grown via gas-timing radio frequency magnetron sputtering and their SERS activity

Pongbordin Ukahapunyakul^{ab}, Nurak Gridsadanurak^{ab*}, Chaweewan Sapcharoenkun^c, Alongkot Treetong^c, Panita Kasamechonchung^c, Pongtanawat Khemthong^c, Mati Horprathum^d, Supanit Porntheeraphat^d, Winadda Wongwiriyan^e, Jiti Nukeaw^e and Annop Klamchuen^{c*}

^a *Department of Chemical Engineering, Faculty of Engineering, Thammasat University, Pathumthani, Thailand,*

^b *Center of Excellence in Environmental Catalysis and Adsorption, Thammasat University, Pathumthani 12120, Thailand*

^c *National Nanotechnology Center (NANOTEC), NSTDA, Thailand Science Park, Pathum Thani, Thailand,*

^d *National Electronics and Computer Technology Center (NECTEC), NSTDA, Pathum Thani, Thailand*

^e *College of Nanotechnology, King Mongkut's Institute of Technology Ladkrabang, Chalongkrung Rd., Ladkrabang, Bangkok 10520, Thailand*

S1. Dependence of peak intensity of (111)/(200) ratio on the resistivity of Ag thin films.

Figure S1 displays the resistivity of Ag thin films as a function of (111)/(200) ratio. The sputtered Ag thin films were deposited on Si (111) substrate. The resistivity of silver thin films is measured by 4-probe measurement (JANDEL model RM3). It can be seen that the resistivity decreases when the peak intensity of (111)/(200) ratio is increased. Since the fine columnar directly relates to the peak intensity of (111)/(200) ratio, the relatively low value of resistivity for sputtered Ag thin films possesses the high orientation of texture resulting from the mobility of adatoms promoted by gas-timing (GT) rf magnetron sputtering technique.^{1,2} The minimum resistivity value of our sputtered Ag thin films (4.33 $\mu\Omega\text{-cm}$) higher than the bulk resistivity value of Ag (1.67 $\mu\Omega\text{-cm}$).^{1,2} This indicates that the traces of oxygen might be contained in Ar atmosphere during sputtering process and incorporated in Ag thin films.

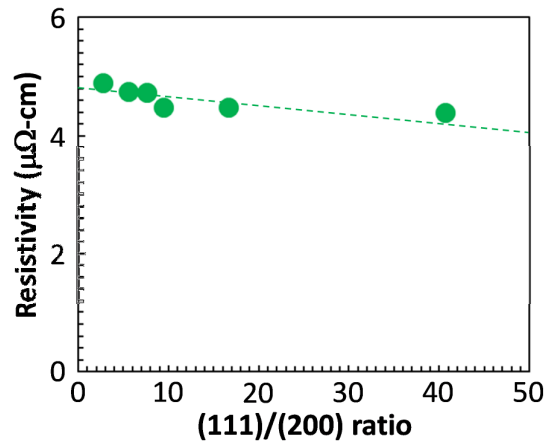


Figure S1 Dependence of peak intensity of (111)/(200) ratio on the resistivity of Ag thin films.

S2. The difference in the deposition rate between turn-on and turn-off gas (ΔR)

Figure S2 demonstrates the difference in the deposition rate between turn-on and turn-off gas (ΔR) as a function of (a) turn-on GT, (b) turn-off GT, (c) RF power and (d) working pressure. The deposition rate of sputtered Ag thin film is collected by thickness monitor (INFICON SQM-160) which is calibrated the thin film thickness via step profiler (MITUTOYO SURFTEST). It can be seen that the ΔR seems to be constant when the turn-on gas sequence is varied whereas the ΔR increases when the turn-off gas sequence is extended as shown in figure S2 (a) and S2 (b), respectively. Figure S2 (c) exhibits the ΔR as a function of RF power. The results show that the ΔR rapidly increases and seems to be saturated above the power of 100 watts. These results are corresponding to figure 2 (c) which shows the threshold of RF power to the enhance of the peak intensity of (111)/(200) ratio due to the minor impact of RF power.^{1,3,4} On the other hand, we find that the working pressure powerfully influences the ΔR . This result correlate with the increase of $|V_{\text{gas on}} - V_{\text{gas off}}|$ in figure 2 (c).

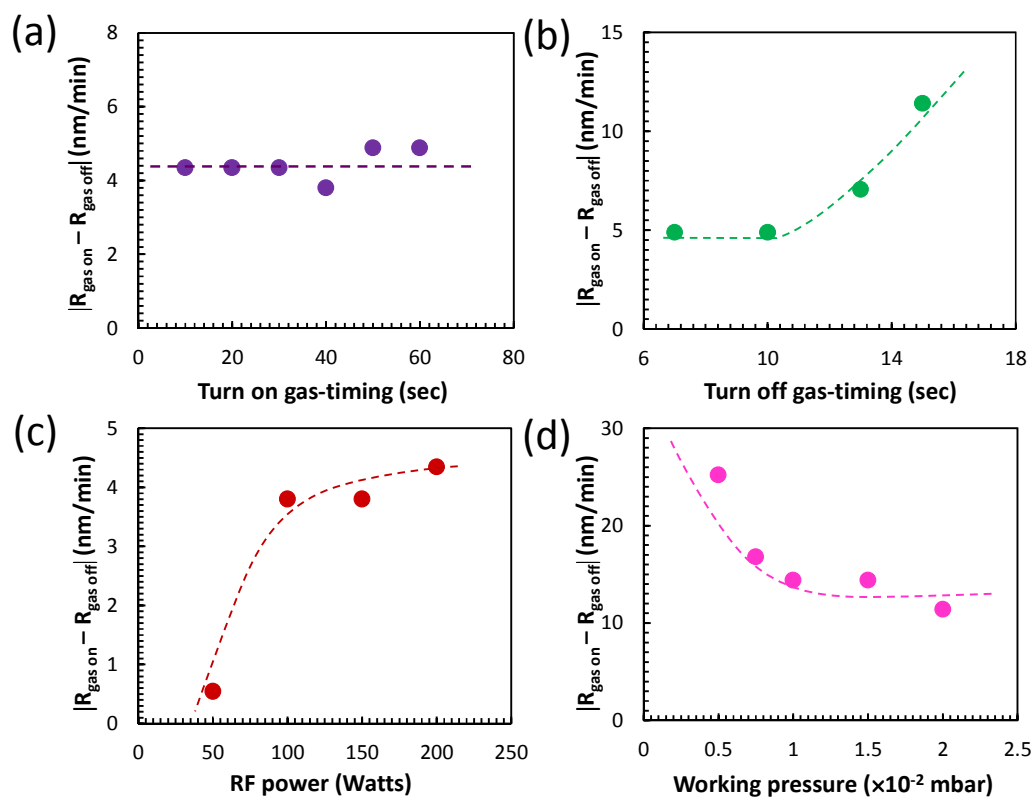


Figure S2 The difference in the deposition rate between turn-on and turn-off gas (ΔR) as a function of (a) turn-on GT, (b) turn-off GT, (c) RF power and (d) working pressure.

S3. Schematic of Ar⁺ and deposition of target atoms using conventional sputtering and GT technique

Figure S3 exhibits the difference of Ar⁺ and deposition of target atoms between conventional sputtering (figure S3 (a)) and GT technique (figure S3 (b)). Within the framework of the sputtering technique, Ar⁺ ions are generated via RF excitation or high voltage between anode and cathode. When Ar⁺ ions are bombarded on the target materials, the energy and momentum transferred to atoms at the surface of target can knock some of these atoms off the target surface. Subsequently, such sputtered atoms travel to a substrate and deposit as a thin film with high kinetic energy. Generally, the sputtered energy in the conventional sputtering is constantly limited by the rf power and working pressure. Therefore, it is very difficult to adjust the sufficient energy for texture orientation. On the other hand, the turn-off gas sequence in GT technique can be attributed, as the reduction of the working pressure. Thus, the decrease of the deposition rate as to the lower amount of sputtered atoms will raise the energy per atom of particles. Such energetic particles will transfer energy and momentum to Ag atoms condensed on the film surface, resulting that the mobility of adatoms can be occurred as following the atomic peening effect as shown in figure S3 (b).

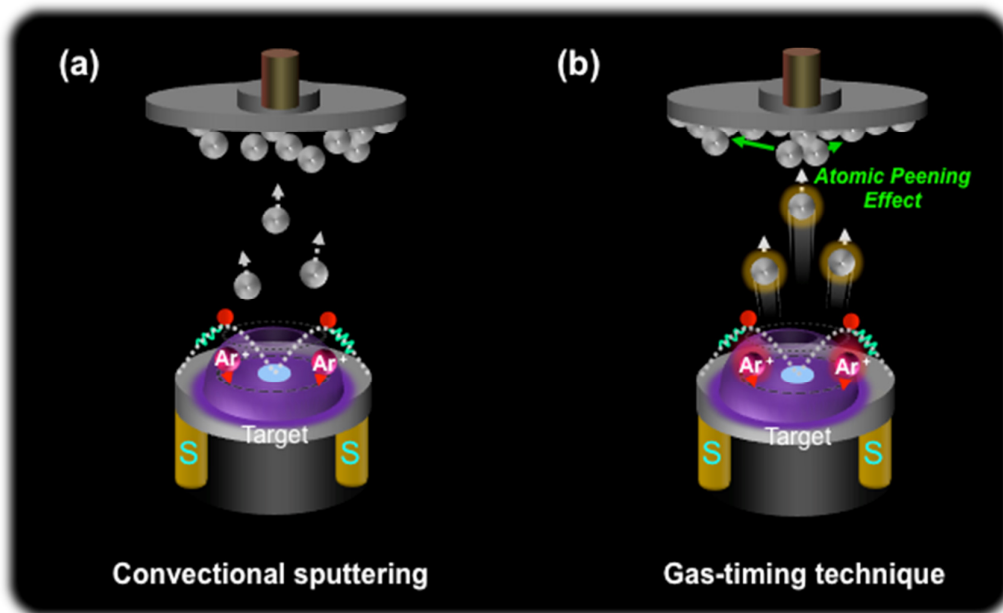


Figure S3 Ar⁺ and deposition of target atoms using (a) conventional sputtering and (b) GT technique.

Reference:

- 1 K.-F. Chiu and Z. H. Barber, *Thin Solid Films*, 2000, 358, 264-269
- 2 P. Catania, R. A. Roy and J. J. Cuomo, *J. Appl. Phys.*, 1993, 74, 1008-1014
- 3 N. Marechal, E. Quesnel, and Y. Pauleau, *J. Vac. Sci. Technol. A*, 1994, 12, 707-713
- 4 N. Marechal, E. Quesnel and Y. Pauleau, *Thin Solid Films*, 1994, 241, 34-38