Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Textile-Based High-Performance Hydrogen Evolution of Low-Temperature Atomic Layer Deposition Cobalt Sulfide

Donghyun Kim,[a] Jeong-Gyu Song,[b] Hyungmo Yang,[c] Hoonkyung Lee,[c] Jusang Park,[a] and Hyungjun Kim*[a]*

[a] School of Electrical and Electronic Engineering, Yonsei University, Seoul 120-749, Korea

[b] Process Technology Group, Samsung Advanced Institute of Technology, 130, Samsung-ro, Yeongtong-gu, Suwon-si, Gyeonggi-do, 443-803, Korea

[c] Department of Physics, Konkuk University, Seoul 05029, Korea

*e-mail: hyungjun@yonsei.ac.kr

A. Growth Characteristics of CoS_x Versus the Number of ALD Cycles

The growth characteristics of ALD CoS_x films are shown in Figure S1. The film thicknesses versus the number of ALD cycles are measured with atomic force microscopy (AFM) and scanning electron microscopy (SEM). The ALD CoS_x film can be observed after 100 cycles of process while the sample of ALD CoS_x 50 cycles seems particle-like morphology as shown in Figure S1(a) and Figure S1(b). The thicknesses of each samples was measured of 3.6 nm in the case of ALD 50 cycles and 8.0 nm in the case of ALD 100 cycles. Figure S2(a) shows the cross image of SEM for measuring the thickness of ALD CoS_x 200 cycles of 13 nm, while the thickness of ALD CoS_x 400 cycles is 26 nm. (Figure S2(b)) From the linear fit of the plots, the growth rate was determined to be about 0.75 Å/cycle, and the growth is almost linear from the initial growth. The linearity of the graph indicates that the CoS_x-film thickness can be precisely controlled by adjusting the number of ALD cycles.

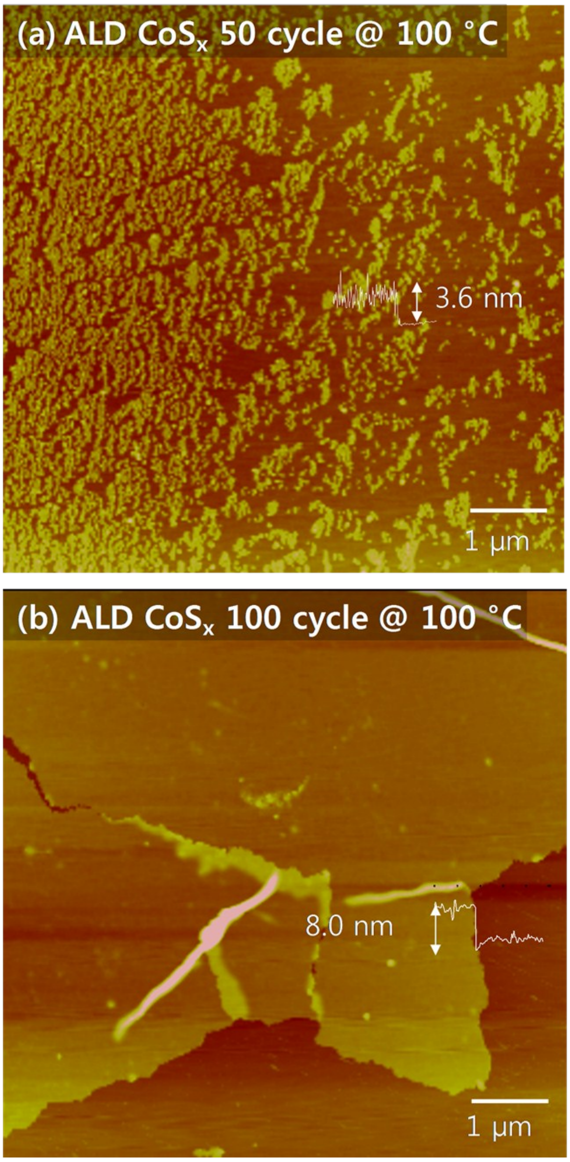


Figure S1. (a) AFM image of ALD CoS_x of 50 cycles and the thickness, (b) AFM image of ALD CoS_x of 100 cycles and the thickness.

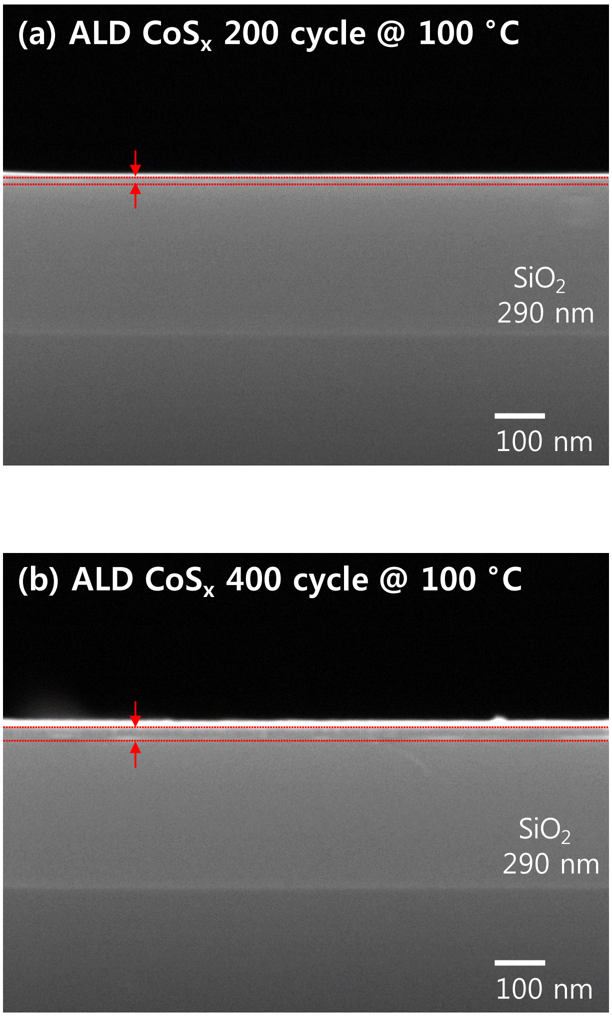
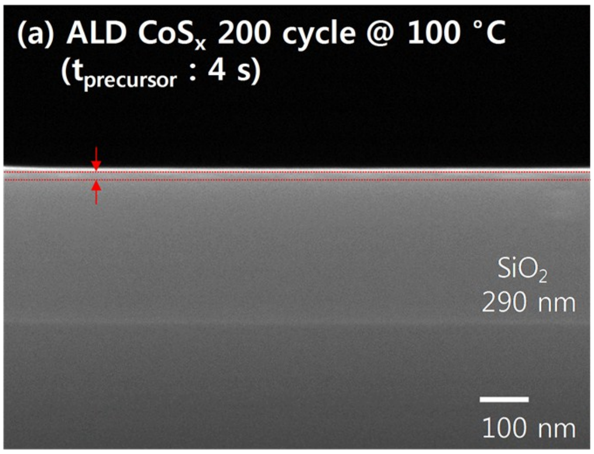


Figure S2. (a) SEM cross image of ALD CoS_x of 200 cycles and the thickness, (b) SEM cross image of ALD CoS_x of 400 cycles and the thickness.

B. Growth Characteristics of ALD CoS_x Versus Precursor Exposing Time

For confirming the CoS_x films were prepared with appropriate ALD process, various samples were deposited with different precursor exposing time, because the unique characteristic of ALD process is known that the growth rate of the film is fixed although the precursor exposing time increases. In this work, the optimized process is composed of 4 steps; a) 4 s of exposing precursor, b) 5 s of purging, c) 4 s of exposing reactant, d) 5 s of purging. The sample were prepared with varying only the precursor time from 2 seconds to 6 seconds with total 200 cycles. In the case of exposing precursor during 2 seconds, the film could not be observed, indicating it was not enough for forming film. Figure S3(a) and Figure S3(b) exhibit the SEM images of ALD CoS_x samples of exposing precursor 4 seconds and 6 seconds. The measured thicknesses of each samples are all the same of 13 nm. The growth rate of the sample is saturated, which confirms that the prepared CoS_x films were deposited with appropriate way of ALD.



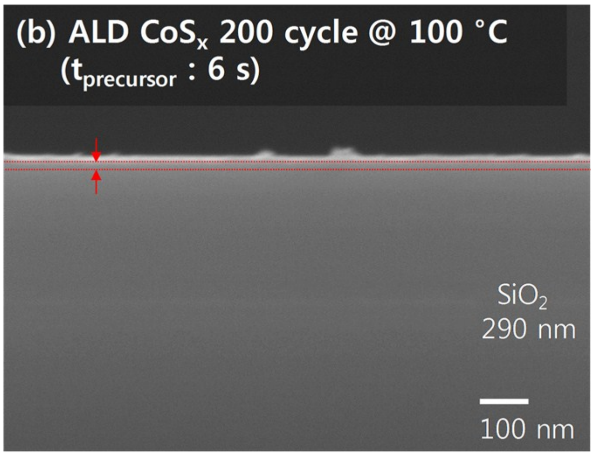


Figure S3. Cross SEM images of ALD CoS_x films with different exposing time of precursor (a) 4 seconds, (b) 6 seconds.

C. HER Performances of ALD CoS_x Depending on Thickness

The HER catalyst based on ALD CoS_x was analyzed with 3 electrode system. Figure S4(a) shows polarization curve of ALD CoS_x depending on the number of cycles. The onset potential and overpotential of the case of the 200 cycles is higher than the case of the 100 cycles. Also, tafel plot shown in figure S4(b) exhibits the case of the ALD CoS_x of 100 cycles is lower tafel slope than the 200 cycles. It indicates that the ALD CoS_x of 100 cycles is more effective catalyst than the ALD CoS_x of 200 cycles. This might due to the way of transferring electron from catalyst to the electrolyte becomes longer.[1]

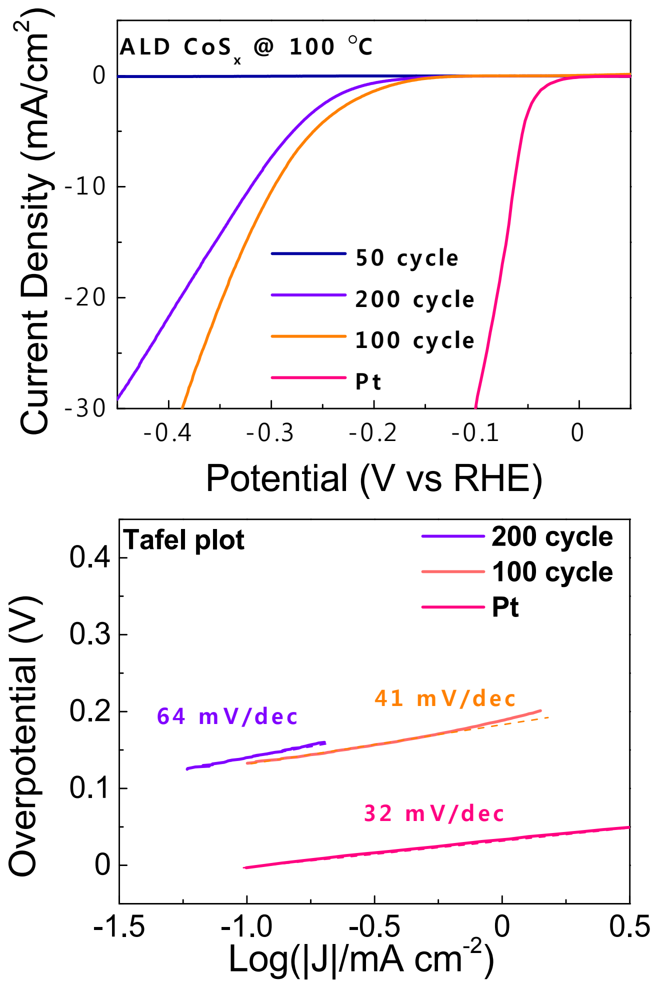


Figure S4. (a) Polarization curve of ALD CoS_x of 100 cycles and 200 cycles, and (b) corresponding tafel plot of the same samples.

D. Comparison with Other HER Catalysts

The ALD CoS_x in this work is compared with other previously reported HER catalysts. It shows lower tafel slope which indicates the kinetic property of the ALD CoS_x is better than the compared catalysts. Also, exchange current density of CoS_x can be enlarged through exploiting the three-dimensional substrate, such as conducting textiles in this work.

Sample	η [mV vs RHE] for J = -10 mA/cm²	Tafel slope [mV/dec]	R_s [Ω cm²]	J_0 [μA/cm²]
CoPS Film	-128	57	2.64	56
CoPS NPls	-48	56	1.42	984
Co/Co_3O_4	-90	44	-	-
CoO_x	~ -200	115	85	
NiMoS/Carbon cloth	-200	85.3	1.9~2.2	48.9
CoS_x/GF*	-295	41	1.74	63.1
CoS_x/CT*	-265	41	1.67	288

Table S1. Comparison with other HER catalysts

E. DFT Calculations

It is demonstrated that ALD CoS_x has optimized hydrogen adsorption energy through density function theory (DFT) calculations. Figure S5 shows the all the calculations carried out for various structures of cobalt sulfides.

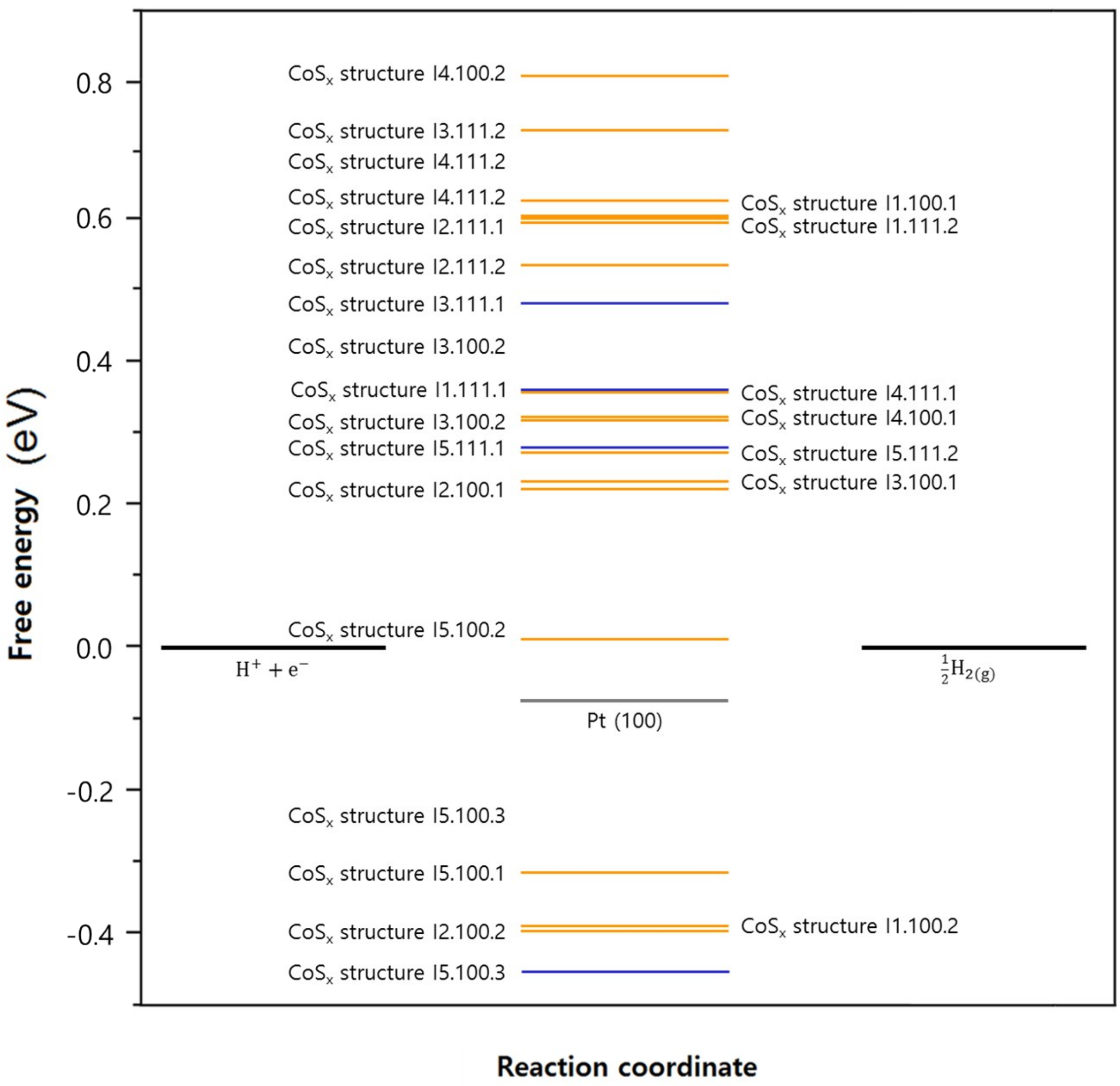


Figure S5. DFT calculation results for various cobalt sulfides.

F. Digital Images of Conductive Textiles

Figure S6 exhibits the prepared samples of ALD CoS_x on conductive textiles. It shows the ALD CoS_x deposited on conductive textiles and woven clothes which is put on a model of a human body.

(a)
(b)

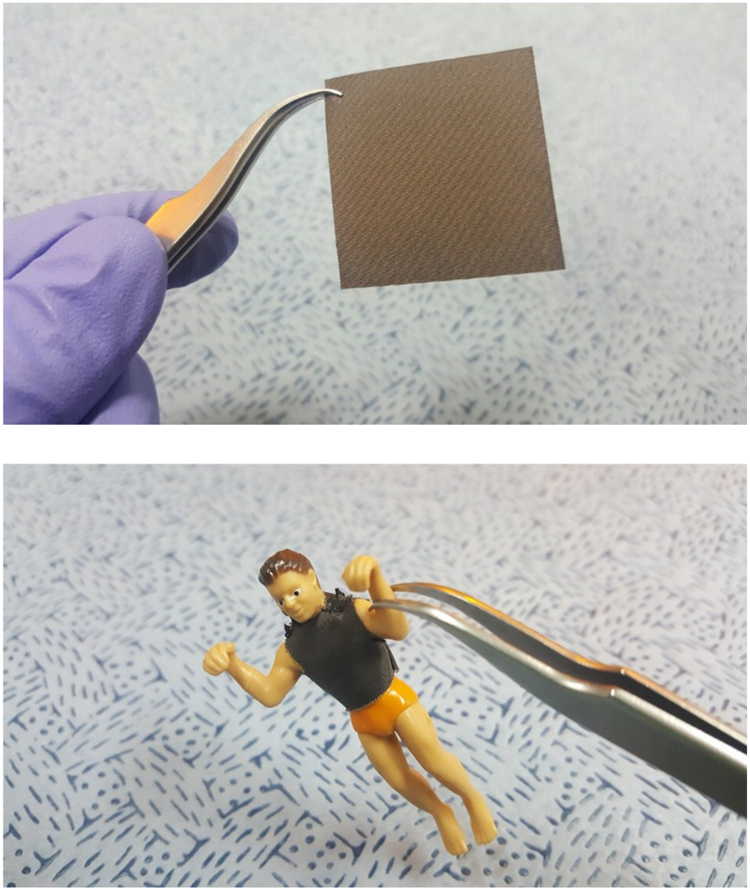


Figure S6. Digital image of (a) a sample of ALD CoS_x on conductive textile with 2 cm × 2 cm size and (b) woven clothes with prepared sample.

G. Surface observation of ALD CoS_x/GF by SEM

To clarify the catalytic performance is mainly affected by phase of the CoS_x, grown CoS_x films on graphite foil (GF) were observed by SEM. The films were grown by ALD of 100 cycles at 100 ˚C and 200 ˚C, respectively. It shows no distinct change of morphology depending on the growth temperature.

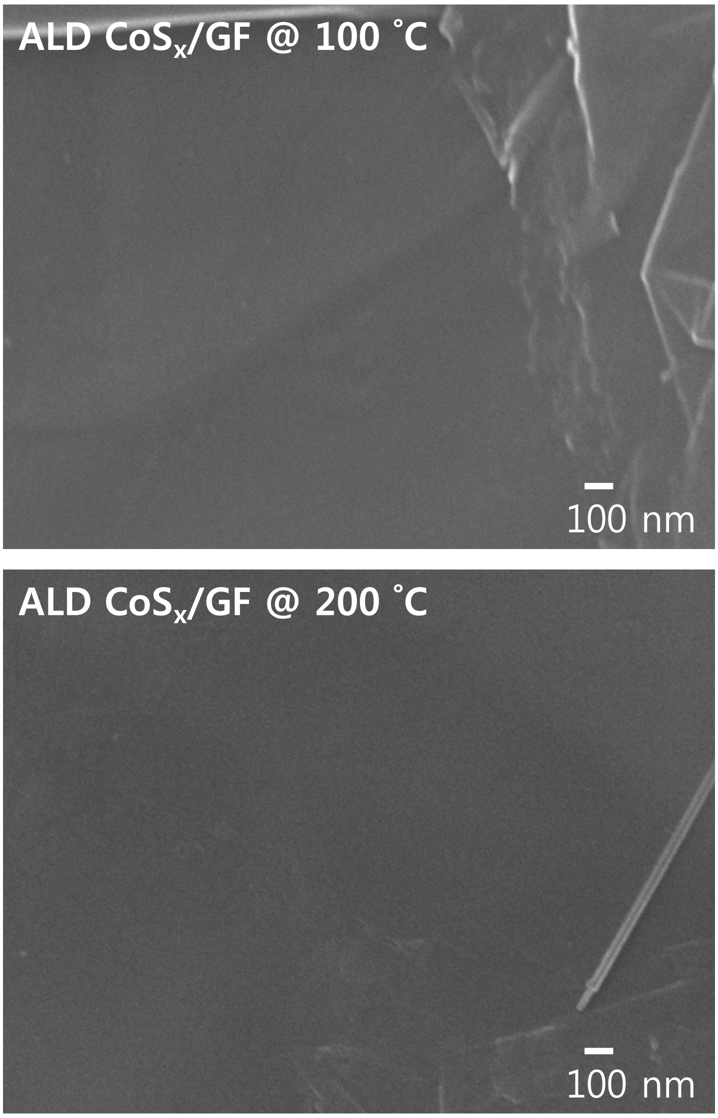


Figure S7. SEM data of ALD CoS_x/GF of 100 cycles at different temperature

Reference

1. Yifei Yu, Sheng-Yang Huang, Yanpeng Li, Stephan N. Steinmann, Weitao Yang, and Linyou Cao, *Nano Lett.*, 2014, **14 (2)**, pp 553–558