Decay dynamics of a monolayer silver film on Si(001)

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Under operando conditions, silicon-based semiconductor devices are subject to impulses from mechanical, thermal, electrical, and photonic excitations, leading inevitably to structural decay.[1–4] The dynamics associated with the decay process (e.g., rate, pathway and barrier) is of practical interest, because it is crucial for stability assessment, lifetime prediction, and performance optimization.

Here, we describe the decay dynamics of a monolayer silver film on Si(001). Extended in-situ monitors of the evolution of (2x2) Ag-film/Si(001), using ultra-high vacuum scanning tunneling microscopy between 245 K and 276 K, demonstrate the thermal decay of the silver film by successive detachment of silver tetramers at the edge of the film (shown in Figure S1a-b of the supplementary pages). Complementary measurements, using the "annealing/quenching" method, gave evidence that the detached silver had transitioned into a mobile state, Ag(m), which is capable of migrating and aggregating into clusters on both bare and silver-covered silicon surfaces (as in Figure S1c of the supplementary pages). Based on these experimental findings, we propose a first-order kinetic model that centers on the reversible transition of silver between the (2x2) Ag-film and Ag(m). By applying this model to our experimental data, an excellent fit can be achieved, yielding an activation of 0.386 ± 0.010 eV for the (2x2) Ag-film to Ag(m) transition, and that of 0.332 ± 0.012 eV for the Ag(m) to the (2x2) Ag-film transition. The obtained pre-exponential factors are anomalously low, i.e. 2067 ± 877 s^{-1} for the (2x2) Ag-film to Ag(m) transition, and 90 ± 47 s^{-1} for the Ag(m) to the (2x2) Ag-film transition. Such low values of the pre-exponential factors are likely linked to an entropic effect, on which density functional theory simulations are underway to provide further insight.

REFERENCE

(1) Huff, T. R.; Labidi, H.; Rashidi, M.; Koleini, M.; Achal, R.; Salomons, M. H.; Wolkow, R. A. Atomic White-out: Enabling Atomic Circuitry through Mechanically Induced Bonding of Single Hydrogen Atoms to a Silicon Surface. *ACS Nano* **2017**, *11* (9), 8636–8642.

(2) Huang, K.; Huang, X.; Nogami, J. Isolated and Assembled Silver Aggregates on the Si(001) Surface: The Initial Stage of Film Formation. *Phys. Chem. Chem. Phys.* **2021**, *23* (7), 4161–4166.

(3) Harikumar, K. R.; McNab, I. R.; Polanyi, J. C.; Zabet-Khosousi, A.; Hofer, W. A. Imprinting Self-Assembled Patterns of Lines at a Semiconductor Surface, Using Heat, Light, or Electrons. *Proc. Natl. Acad. Sci.* **2011**, *108* (3), 950–955.

(4) Dobrin, S.; Lu, X.; Naumkin, F. Y.; Polanyi, J. C.; Yang, J. S. Y. Imprinting Br-Atoms at Si (1 1 1) from a SAM of CH_3Br (Ad), with Pattern Retention. *Surf. Sci.* **2004**, *573* (2), L363–L368.

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Supplementary Pages (Optional)

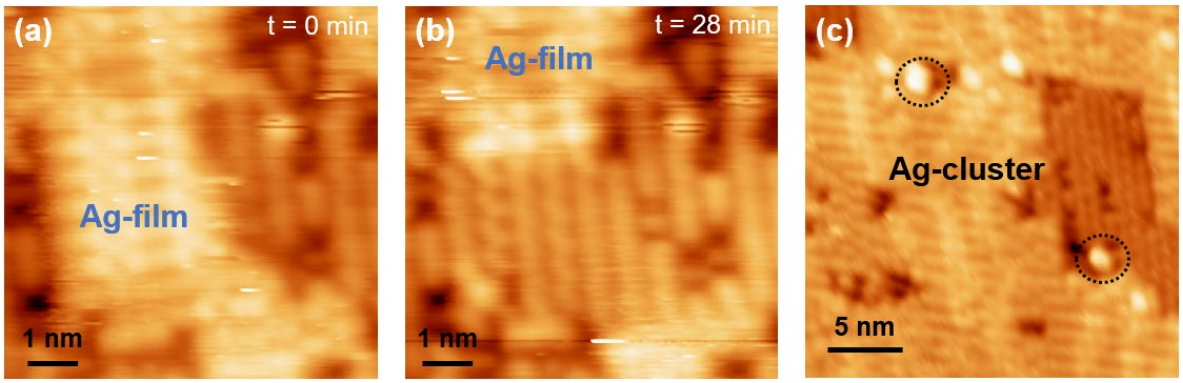

Figure S1. Panel (a)-(b) demonstrate the decay of a patch of the (2x2) Ag-film on Si(001) over 28 min at 245 K. (c) Formation of Ag-clusters upon the the decay of (2x2) Ag-film on Si(001).