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Ultrathin two dimensional metals with fully exposed (111) facets

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Methods

Materials. Pt, Au and Ag sputtering targets of with a purity of 99.99% were purchased from China Mew Metal Materials Technology Co., Ltd. Polished Si (100), Si (111) Si/SiO_2 substrates (0.5 mm or 1.0 mm in thickness, 10 mm ×10 mm, 300 nm for SiO_2 layer) were purchased from Hefei Kejing Materials Technology Co., Ltd. Trimethylchlorosilane (>99.0%) was purchased from Sigma-Aldrich. All chemicals used in this study were used as received without further purification.

Sample Preparation. Ultrathin Pt metal films were deposited on Si or Si/SiO_2 substrates by a conventional DC magnetron sputtering system with high-purity Pt target. The deposition was carried out with flowing gas of 0.20 sccm and ambient pressure of 0.30 Pa at a typical deposition rate of 5.5 Å s^{-1}. Then, as-sputtered Pt film on polished Si substrate was covered by another piece of Si substrate (with polished side being downward and passivated by trimethylchlorosilane in advance) and then transferred into the work platform of heat-press machine (AS ONE HP-3P, AH-4105). The stacked silicon wafers were further heat-pressed in a typical process. Once the temperature increasing to 250 ^{o}C, the loading press was gradually boosted from 0 to 0.30 GPa and remained at 0.30 GPa for 30 min, and it was allowed to release the pressure and separate the pair of Si substrates after cooling to room temperature naturally (similar conditions for 2D Au and Ag, except that the deposition rate was controlled to be 8 and 12 Å s^{-1} as well as the peak temperatures were changed to 300 and 200 ^{o}C, respectively).

Characterization. X-ray diffraction (XRD) patterns were acquired using a D/MAX 2500 diffractometer (Rigaku, Japan) attached with Cu Kα radiation. SEM images were taken with a Zeiss Field emission scanning electron microscopy (FESEM, MERLIN VP Compact, Germany). High resolution transmission electron microscopy (HR-TEM) on a JEM-ARM200F operated at 200 kV were used to study the morphology and crystallinity of metal samples peeled from substrates by diluted HF etching. The thickness of ultrathin metal film was examined by an atomic force microscopy (AFM, SPM-9600, SHIMADZU Corporation) in the tapping mode. X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo Scientific ESCALAB 250Xi with Al Kα (1487.6 eV) as the excitation source and C 1s peak (284.8 eV) as the calibration. Electron backscatter diffraction (EBSD) image was acquired from a scanning auger nanoprobe spectrometer (AES, PHI 710). The sheet resistances of ultrathin metals on Si/SiO_2 substrates were measured in their flat state by using a multifunctional four-point probe tester (ST-2258C, Suzhou Jingge Electronic Co., LTD, China).

Electrochemical measurements. The methanol electro-oxidation reaction measurements were carried out in 0.1 M $HClO_4$ solution containing 1.0 M methanol at room temperature. A conventional three-electrode system was controlled by a CHI660E electrochemical analyzer, using Pt covered Si slices connected with stainless steel electrode holder as working electrode, Ag/AgCl electrode as the reference electrode, Pt mesh as the counter electrode. For MOR stability tests, CV sweepings

were conducted with a scanning rate of 50 mV s^{-1} for 200 cycles. Before each measurement, dozens of cycles were performed in pure 0.1 M $HClO_4$ solution until stable CV curves were obtained. All potentials measured were calibrated to the reversible hydrogen electrode (RHE) using the following equation: $E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059 \times pH$.

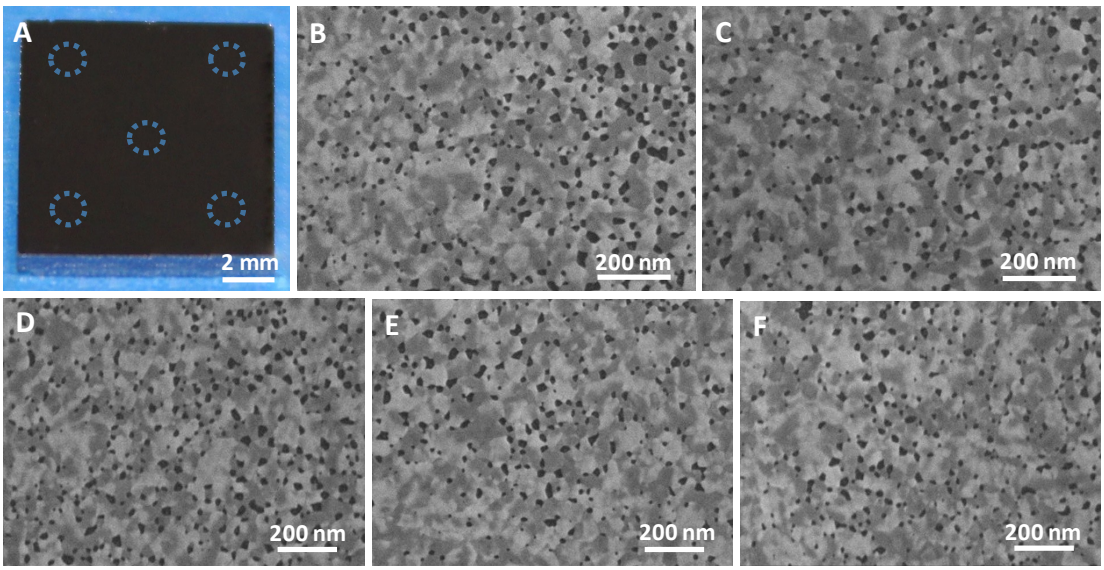

Fig. S1 (A) Optical photograph of Pt 5 nm heat-pressed on Si (100) substrate. (B), (C), (D), (E) and (F) SEM images of Pt 5 nm after heat-pressing at a magnification of 100K from different areas in book fashion as marked in (A).

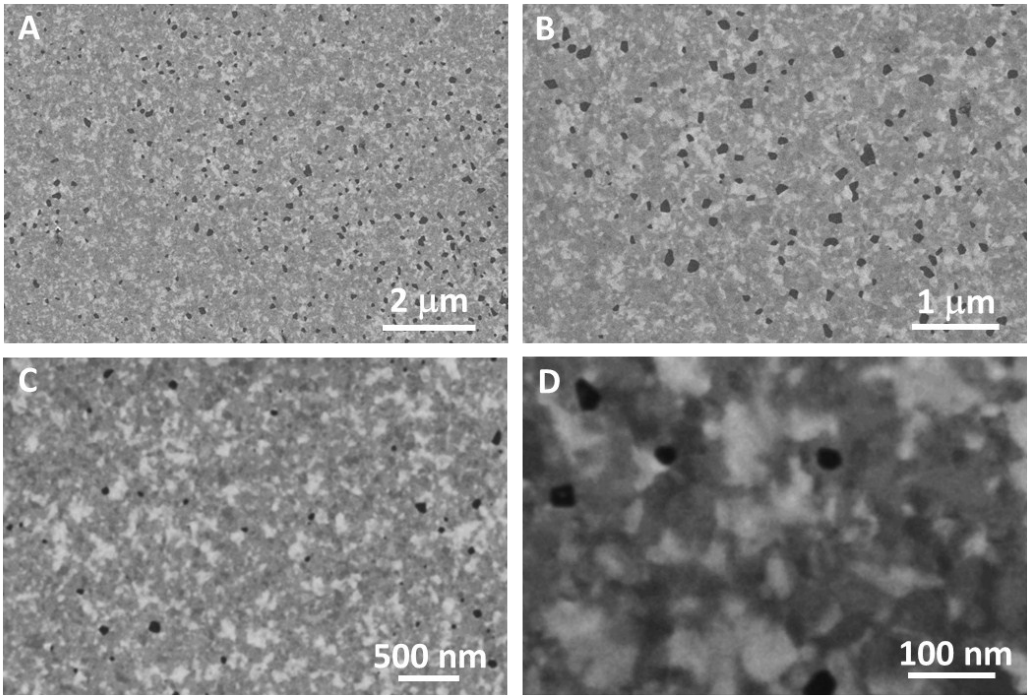

Fig. S2 SEM images of Pt 10 nm after heat-pressing at different magnifications.

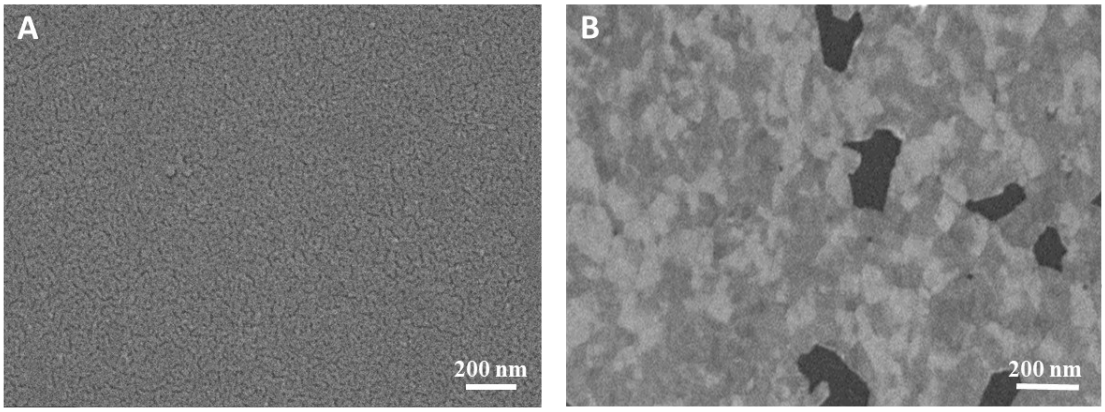

Fig. S3 SEM images of Au 10 nm before and after heat-pressing at 300 ℃.

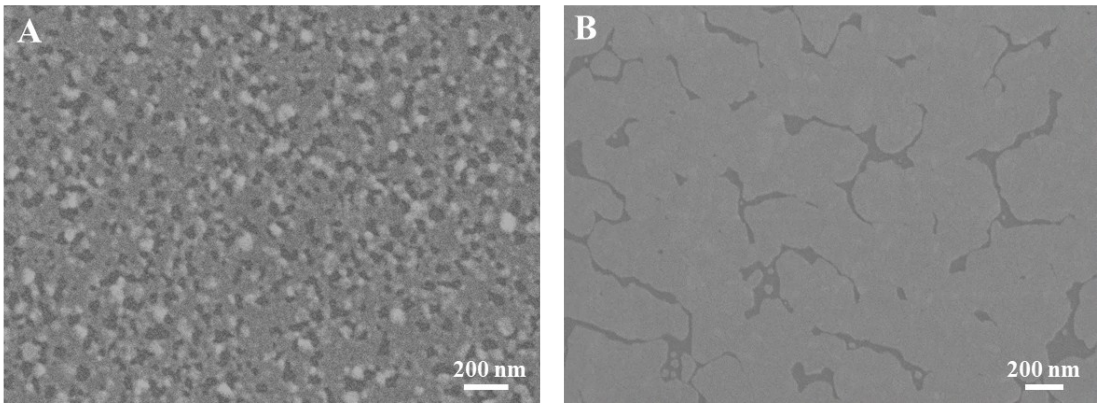

Fig. S4 SEM images of Ag 10 nm before and after heat-pressing at 200 ℃.

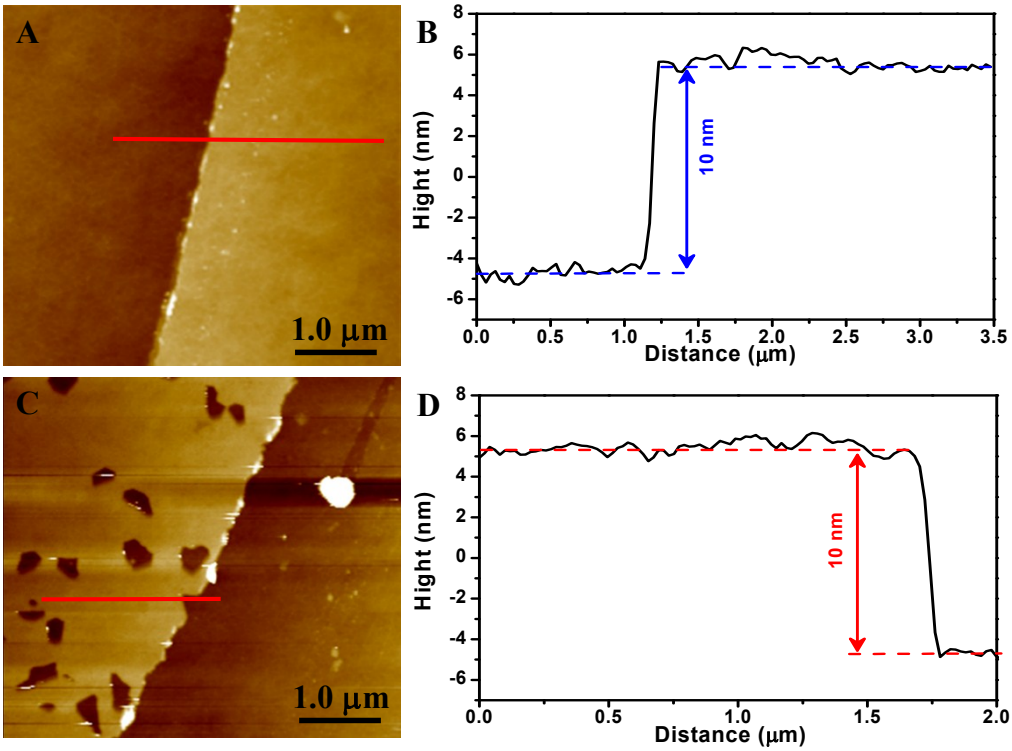

Fig. S5 AFM images of Au 10 nm before (A and B) and after (C and D) heat-pressing at 300 ℃.

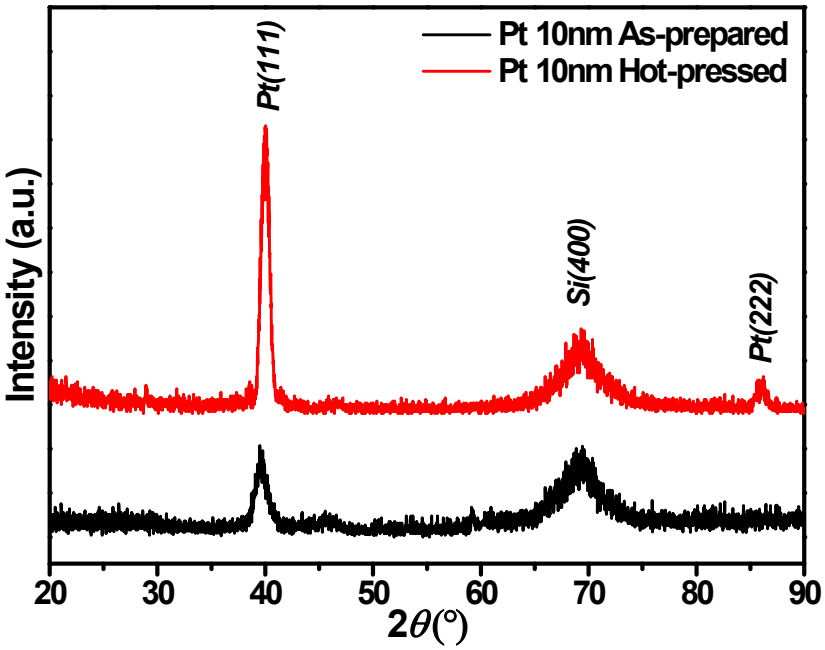

Fig. S6 XRD patterns of Pt 10 nm on Si (100) before and after heat-pressing at 250℃.

The small peak shifts of Pt(111) can be attributed to the lattice distortion caused by internal residual stresses during heat-pressing process.

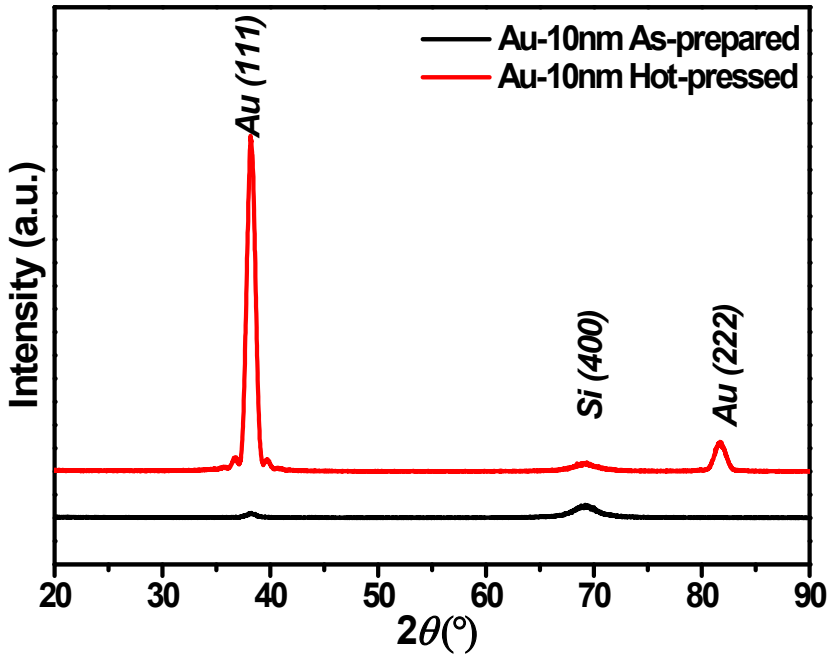

Fig. S7 XRD patterns of Au 10 nm on Si (100) before and after heat-pressing at 300 ℃.

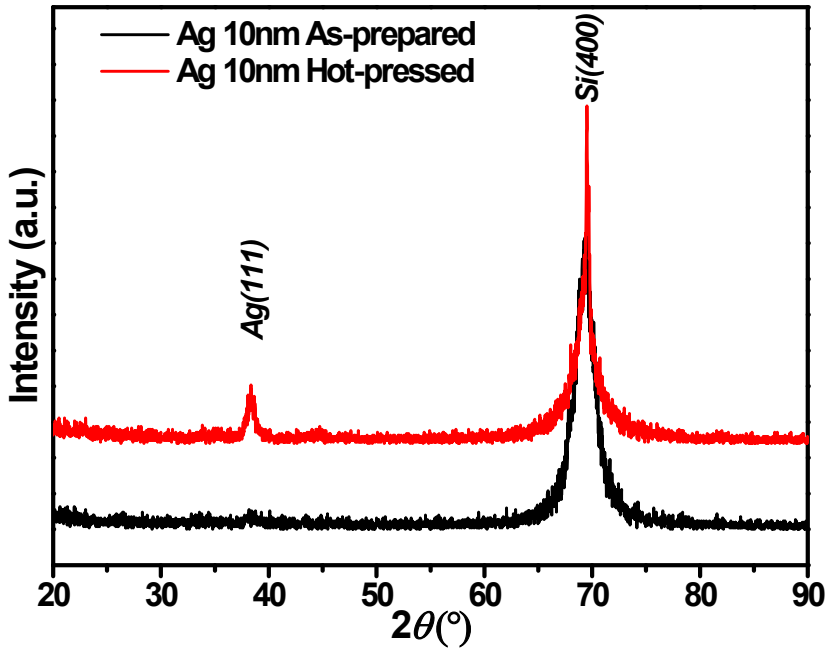

Fig. S8 XRD patterns of Ag 10nm on Si (100) before and after heat-pressing at 200 ℃.

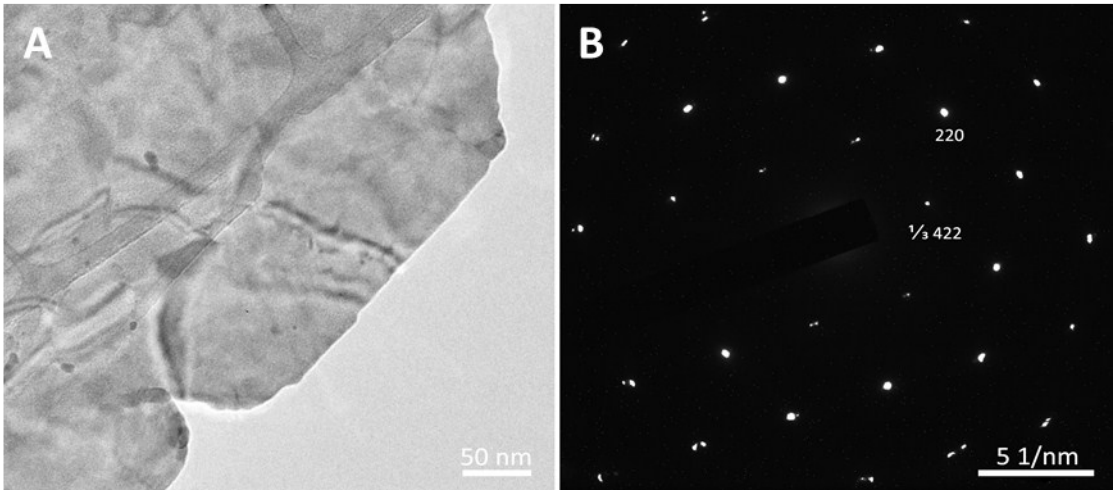

Fig. S9 TEM and corresponding SAED pattern of Pt 5 nm film after heat-pressing. The presence of the forbidden diffraction spots of 1/3{422} planes can be attributed to several possible reasons, such as the small thickness of the crystal with an atomic layer number that is not an integral multiple of 3, or the presence of stacking faults parallel to the (111) basal plane.

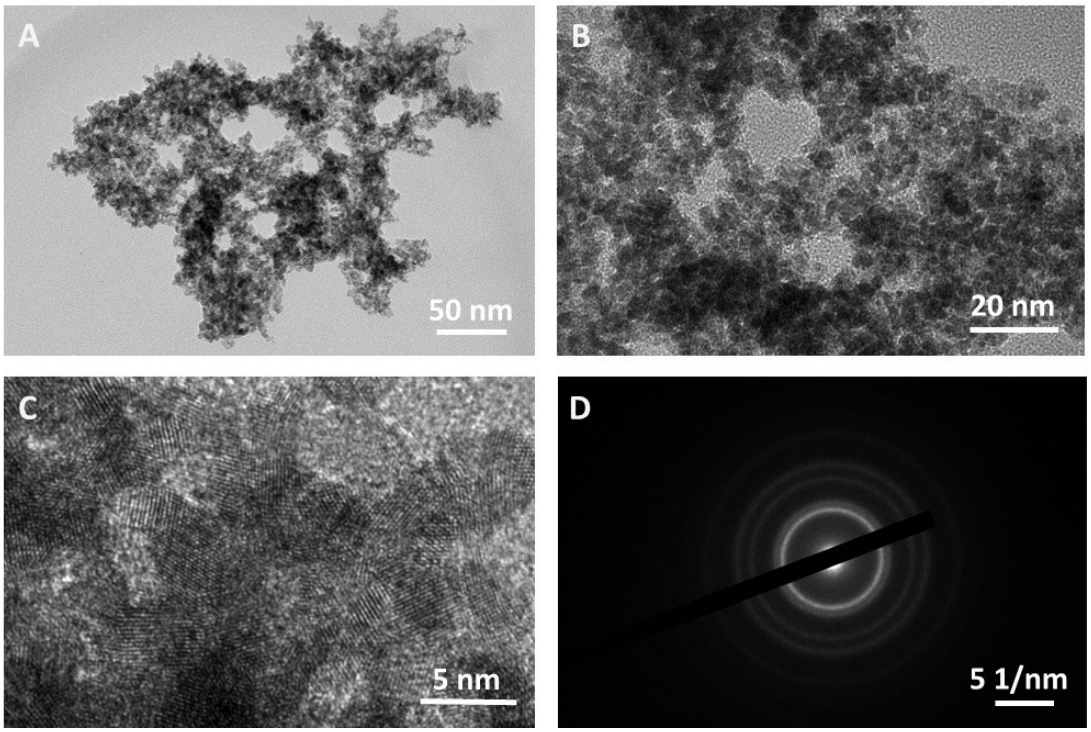

Fig. S10 TEM (A, B) and HR-TEM (C) images of as-sputtered Pt 5nm films peeled off form Si wafer by HF etching, and corresponding electron diffraction pattern (D).

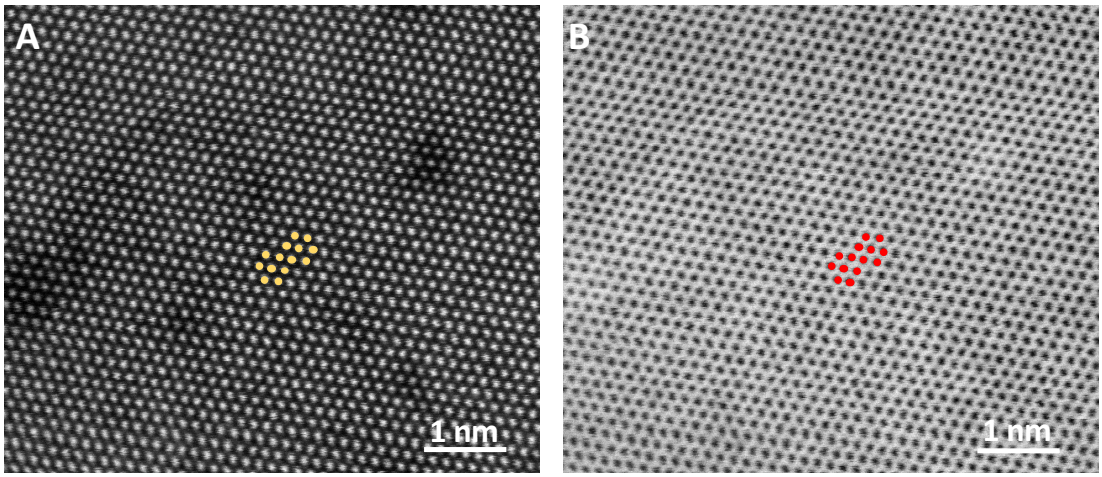

Fig. S11 (A) High-angle annular dark-field (HAADF) image and (B) Atomic-resolution annular bright-field (ABF) image of 2D Pt 5 nm, where Pt atoms were indicated by yellow and red filled circles, respectively.

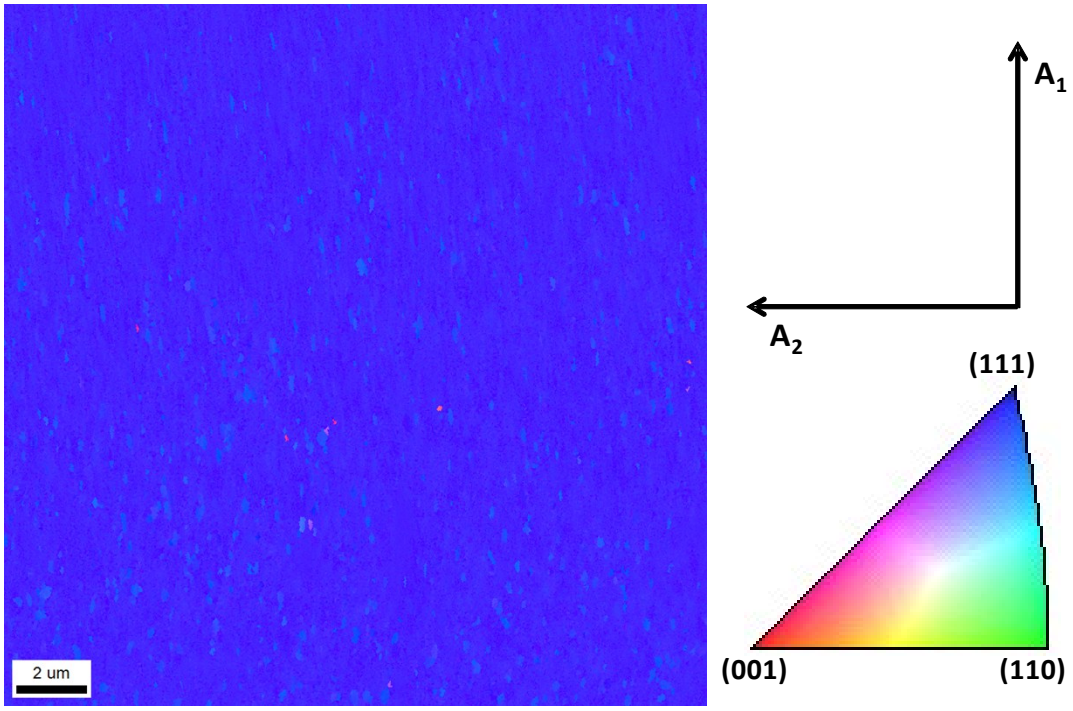

Fig. S12 EBSD image of Pt 5nm heat-pressed on Si (100) substrate. Color code map type: Inverse pole figure [001].

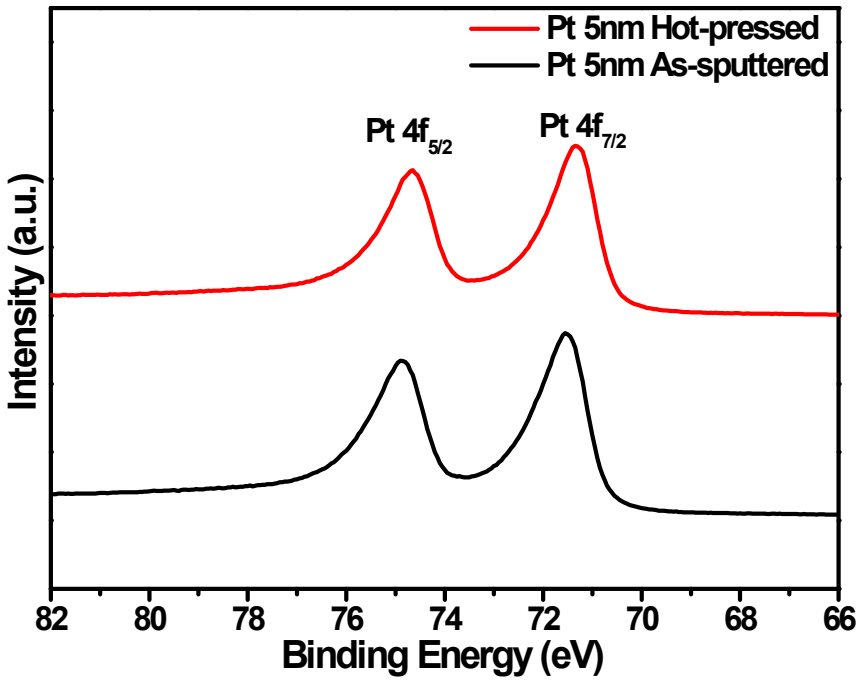

Fig. S13 XPS spectra for Pt 4f photoemission from Pt 5nm on Si (100) before and after heat-pressing process at 250 ℃.

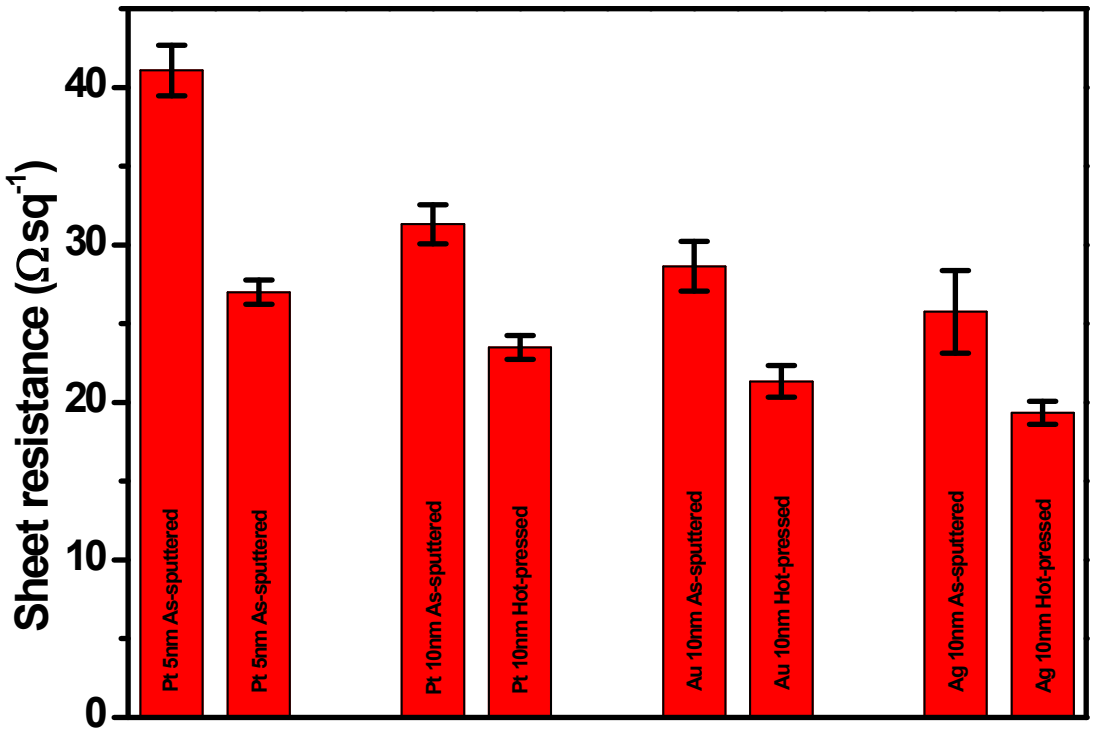

Fig. S14 Sheet resistance changes for ultrathin 2D Pt, Au and Ag by heat-pressing.