Improvement of Metal-Semiconductor Contact from Schottky to Ohmic by Cu Doping in Transition Metal Dichalcogenide Transistors

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Abstract—Metal-semiconductor (MS) contacts were changed from Schottky to Ohmic in synthesized tungsten disulfide (WS_2), due to Cu doping during the synthesis. Significant reductions of contact barrier and resistance were achieved. A statistical study shows transistor performance including carrier mobilities, on/off ratios, on-current densities, and subthreshold swings were also improved significantly with Cu doping.

I. INTRODUCTION

Two-dimensional (2D) layered crystals such as transition metal dichalcogenides (TMDs) have strong in-plane covalent bonding and weak out-of-plane van der Waals (vdW) interaction. Theoretical models predict that among various semiconducting TMDs, WS_2 has the highest electron mobility and the best transistor performance including the highest on/off ratios and on-current densities [1, 2]. However, to apply WS_2 into complementary metal-oxide-semiconductor logic circuits, contact engineering is highly required [3-5]. In this work, we report significantly improved performance of few-layer WS_2 field-effect transistors (FETs) by Cu doping. Compared to pristine-WS_2 FETs, the Cu-doped WS_2 (Cu-WS_2) devices show a notable reduction of MS barrier height and contact resistance, and a Schottky-to-Ohmic contact improvement. Transistor performance, including carrier mobilities (μ_{FE}), on/off ratios, on-current densities ($J_{D,on}$), subthreshold swings (SS) were also improved considerably based on a statistical study. This work has demonstrated the potential of metal doping for 2D material engineering and device applications.

II. MATERIAL SYNTHESIS AND DEVICE FABRICATION

Both pristine-WS_2 and Cu-WS_2 are synthesized by chemical transport reaction in a two-zone oven, as shown in Fig. 1. The pristine-WS_2 uses S and W as sources; in contrast, the Cu-WS_2 has 0.5 wt. % of Cu foil in addition to S and W sources. The transport reaction runs at 1060 K in an evacuated silica ampoule at a pressure of 10^{-2} Pa and with a temperature gradient of 5.6 K/cm. Cu forms compounds CuI and is transported to the colder side of the ampoule. After 21 days of growth the silica ampoule was slowly cooled to room temperature with a controlled cooling rate of 30 °C per hour.

After synthesis, the flakes are mechanically exfoliated and transferred onto a Si substrate which has a 90-nm-thick SiO_2.

The source and drain electrodes, Ti (10 nm)/Au (100 nm), are patterned by electron beam lithography and deposited by electron beam evaporation. All the devices have the channel length (L) of 1 μm and various channel widths (W). The measurements are performed in a dark N_2 ambient. Drain current (I_D) is measured at various drain voltages (V_D) and back-gate voltages (V_{BG}), and normalized to obtain drain current density ($J_D=I_D/W$) for comparison.

III. RESULTS AND DISCUSSION

Raman spectra (488 nm, 1.5 mW) for both pristine-WS_2 and Cu-WS_2 samples indicate two peaks: in-plane vibration (E^1_{2g}) peak at ~357 cm^{-1} and out-of-plane vibration (A_{1g}) peak at ~423 cm^{-1}, as shown in Fig. 2 (a). No peak shift is detected with Cu doping, indicating that the physical structure of WS_2 is not affected by Cu doping in the van der Waals (vdW) gaps. Both the peak intensity ratios ($E^1_{2g}/A_{1g} < 1$) suggest few-layer structures, which are also confirmed by atomic force microscope (AFM). The flake thickness is ~4 nm for the pristine-WS_2 FET and ~6 nm for Cu-WS_2 FET, as shown in Fig. 2 (b).

Output characteristics (J_D-V_D) and transfer characteristics (J_D-V_{BG}) of pristine-WS_2 FET are shown in Fig. 3. At room temperature, pristine-WS_2 is n-type doped and shows electron transport. A non-linear I-V relation at small V_D indicates a Schottky contact between Ti and pristine-WS_2. The lowest SS and highest μ_{FE} are 2.3 V/dec and 4.9 cm^2/Vs, respectively. According to the hysteresis of charge neutral point (ΔV_{CNP}), the effective trap density (n_t) is estimated as $n_t = C_{ox} \cdot \Delta V_{CNP}/q = 3.1 \times 10^{12}$ cm^{-2}, where C_{ox} is the oxide capacitance (3.83×10^{-8} F/cm^2), and q is the electronic charge. As a comparison, J_D-V_D and J_D-V_{BG} of Cu-WS_2 FET are shown in Fig. 4. The linear I-V relation at small V_D suggests an Ohmic contact between Ti and Cu-WS_2, which is significantly improved compared to pristine-WS_2. Moreover, the Cu-WS_2 FET shows a clear current saturation at large V_D, which is not seen in pristine-WS_2 FET. The lowest SS, highest μ_{FE}, and n_t of Cu-WS_2 FET are obtained as 2.4 V/dec, 21.9 cm^2/Vs, and 3.4×10^{12} cm^{-2}, respectively.

Temperature-dependent electronic transport is investigated in the temperature (T) range from 218 to 298 K. Transconductance (g_m) as a function of V_{BG} for pristine-WS_2 FET is shown in Fig. 5 (a). A crossover from an insulating regime

(increase of g_m with increasing T) to a metallic regime (decrease of g_m with increasing T) is observed at around at ~10 V. This metal-insulator transition (MIT) point corresponds to 2D carrier density ($n_{2D} = C_{ox} \cdot V_{BG}/q$) of 2.4×10^{12} cm^{-2}, and it is the direct consequence of quantum interference effects (QIEs) of weak localization at low carrier densities ($V_{BG} < 10$ V) and strong localization at high carrier densities ($V_{BG} > 10$ V) [2]. Similar MIT behavior has also been found in MoS$_2$ devices [6]. Activation energy (E_a) is estimated by fitting g_m with the expression $g_m = g_{m0} \cdot \exp[-E_a/(k_B T)]$, as shown in Fig. 5 (b), where g_{m0} is a constant, and k_B is the Boltzmann constant. The E_a corresponds to the thermal activation of charge carriers at the Fermi energy into the conduction band, and its dependence on V_{BG} can be used to extract the density of states (DOS) as $(dV_{BG}/dE_a-1) \cdot C_{ox}/q^2$. The maximum DOS is on the order of 10^{14} eV^{-1} cm^{-2}, which is consistent with the theoretical calculation (2.85×10^{14} eV^{-1} cm^{-2}) [2], as shown in Fig. 5 (c). The MS barrier height (ϕ_{MS}) is also estimated based on a thermal emission dominated I-V relation as $J_D \propto T^2 \cdot \exp[-\phi_{MS}/(k_B T)]$ assuming $\exp[-qV_D/(k_B T)] \ll 1$ [7], as shown in Fig. 5 (d). Both the E_a and ϕ_{MS} are consistent with each other, suggesting that the carrier transport is limited by the MS contact. As a comparison, Cu-WS$_2$ FET shows the MIT transition at ~5 V, which corresponds to n_{2D} of 1.2×10^{12} cm^{-2}, as shown in Fig. 6. The maximum DOS is also on the order of 10^{14} eV^{-1} cm^{-2}. In the insulating regimes, the maximum E_a and ϕ_{MS} in Cu-WS$_2$ is about ~300 meV, which is less than pristine-WS$_2$ (~400 meV). This reduced MS barrier height interprets the improvement of contact condition from Schottky to Ohmic by Cu doping.

To further investigate the impact of Cu doping on MS contacts, energy band diagrams are illustrated in Fig. 7. Both the few-layer pristine-WS$_2$ and Cu-WS$_2$ have the bandgap (E_g) of ~1.3 eV and the electron affinity (χ) of 3.9 eV [8]. The workfunction (ϕ_S) is estimated as ~4.3 eV for pristine-WS$_2$ and ~4.1 eV for Cu-WS$_2$. The smaller ϕ_S in Cu-WS$_2$ is due to the electron transfer and chemical interaction between Cu and chalcogenide layers, which increases the Fermi energy and carrier density [3-5]. Due to a gate-controlled Schottky barrier modulation in TMDs [9, 10], ϕ_{MS} depends linearly on V_{BG} when V_{BG} is smaller than the flatband voltage (V_{FB}), and the charge injection through the barrier is dominated by thermionic emission. When V_{BG} is larger than V_{FB}, ϕ_{MS} should not change with V_{BG} and thus deviates from this linear relation. The charge injection in this region is dominated both thermionic emission and Fowler-Nordheim (F-N) tunneling [6], and the further decrease of ϕ_{MS} value is due to the thinning of Schottky barrier. The ϕ_{MS} at V_{FB} (ϕ_{MS0}) for both pristine-WS$_2$ and Cu-WS$_2$ are extracted at the point where ϕ_{MS} stops depending linearly on V_{BG}, as shown in Fig. 8. It is also noted that a Schottky barrier lowering occurs with the increasing V_D due to an image-forces-induced underestimation of ϕ_{MS0}. This can be eliminated by plotting ϕ_{MS0} as a function of V_D and then extracting ϕ_{MS0} at zero V_D by a linear extrapolating [7]. The ϕ_{MS0} is 116 and 92 meV for pristine-WS$_2$ and Cu-WS$_2$, respectively. These values are smaller than the results from density functional theory (DFT) calculation for 1L-WS$_2$ [11], due to the much larger E_g (~2.1 eV) of single layer form.

Temperature-dependent μ_{FE} in Cu-WS$_2$ FET is extracted from g_m, which is about 5 times higher than pristine-WS$_2$, as shown in Fig. 9. The dependence of μ_{FE} on T follows a power-law as $\mu_{FE} \propto T^\kappa$. The temperature damping factor κ is 0.72 for pristine-WS$_2$ and 0.70 for Cu-WS$_2$, suggesting that the Cu doping has negligible effect on charge impurity scattering or screening [2].

Contact resistance (R_c) is extracted from a combination of two-contact and four-contact measurements, as shown in Fig. 10. Compared to pristine-WS$_2$, R_c in Cu-WS$_2$ is about 3 orders of magnitude lower at low carrier densities ($V_{BG} = 10$ V), and about 1 order lower at high carrier densities ($V_{BG} = 30$ V). Besides, channel resistivity ($\rho^{2D}_{channel} = R_{ch} \cdot W/L$) is also obtained, which is superior to 1L-WS$_2$ and comparable with chemically doped few-layer WS$_2$ [7].

A statistical study of transistor performance is carried out for 26 pristine-WS$_2$ FETs and 29 Cu-WS$_2$ FETs, as shown in Fig. 11. Due to the Cu doping, the mean values of μ_{FE}, on/off ratios, and $J_{D,on}$ are about 5, 4 and 2 times increased, respectively; the mean SS is over 30% decreased.

IV. Concluson

The significant improvement of MS contact from Schottky to Ohmic in WS$_2$ FETs was obtained by Cu doping. The average carrier mobilities, on-current densities, on/off ratios, *etc.* were all increased to 10.1 cm^2/Vs, 1.2 µA/µm, and 2.5×10^6, respectively.

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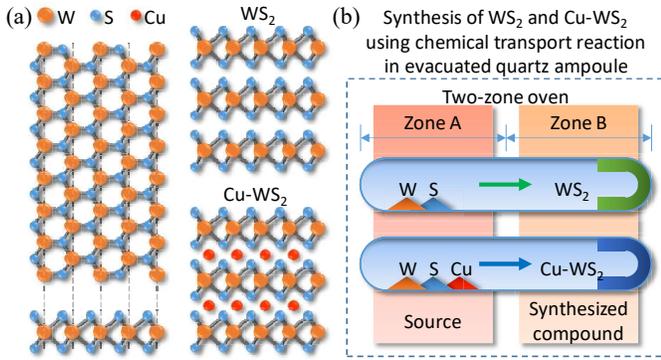
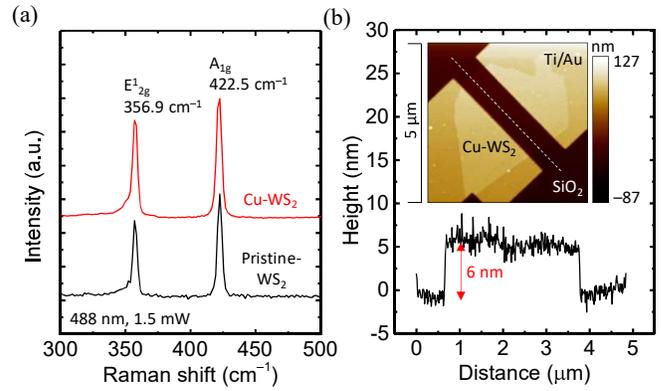Fig. 1. (a) Atomic structure of WS₂ and Cu-WS₂. (b) Schematic of material synthesis using chemical transport reaction.

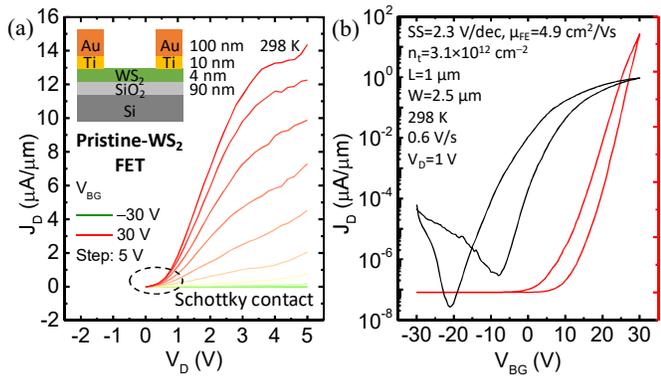Fig. 2. (a) Raman spectrum of few-layer pristine-WS₂ and Cu-WS₂. (b) AFM characterization of a few-layer Cu-WS₂ FET.

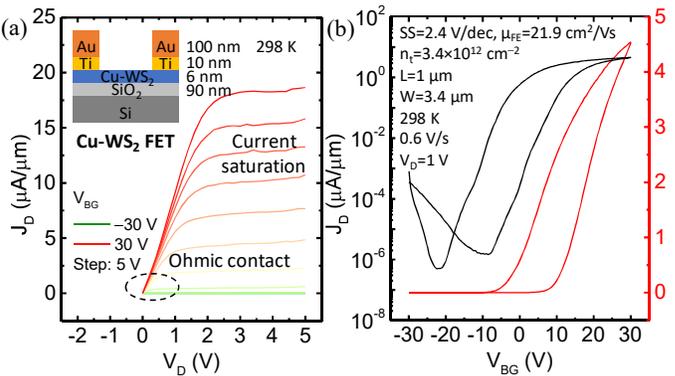Fig. 3. (a) J_D-V_D and (b) J_D-V_{BG} characteristics of pristine-WS₂ FET at room temperature.

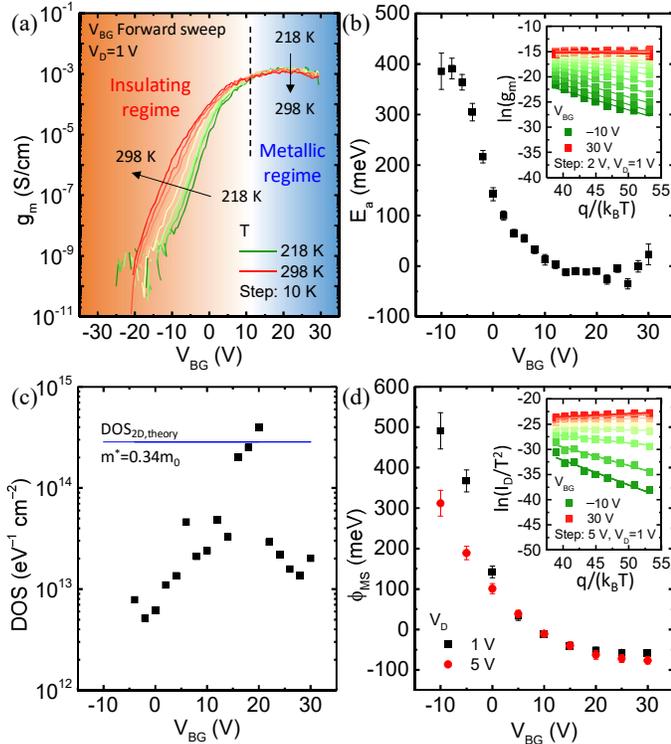Fig. 4. (a) J_D-V_D and (b) J_D-V_{BG} characteristics of Cu-WS₂ FET at room temperature.

Fig. 5. (a) g_m, (b) E_a, (c) DOS, and (d) ϕ_{MS} as functions of V_{BG} in pristine-WS₂ FET.
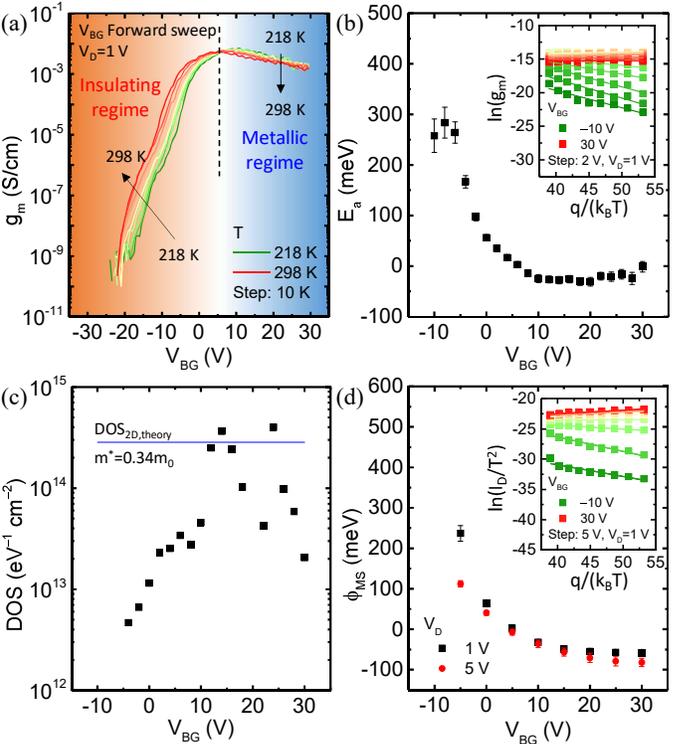
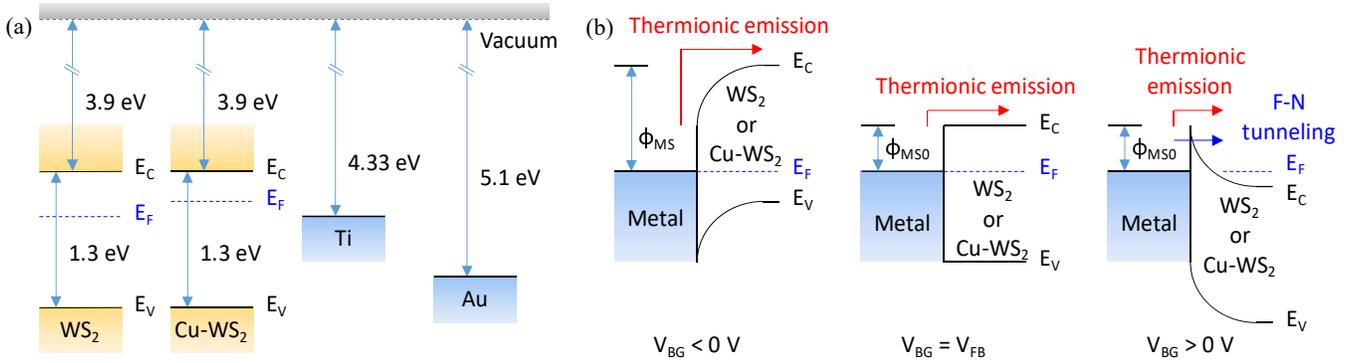Fig. 6. (a) g_m, (b) E_a, (c) DOS, and (d) ϕ_{MS} as functions of V_{BG} in Cu-WS₂ FET.

Fig. 7. (a) Energy band diagram of pristine-WS$_2$, Cu-WS$_2$, Ti, and Au. (b) MS contact barriers at different V_{BG}, including $V_{BG} < 0$ V, $V_{BG} = V_{FB}$, and $V_{BG} > 0$ V. Here E_F is the Fermi energy level, E_C and E_V are conduction band and valence band, respectively.
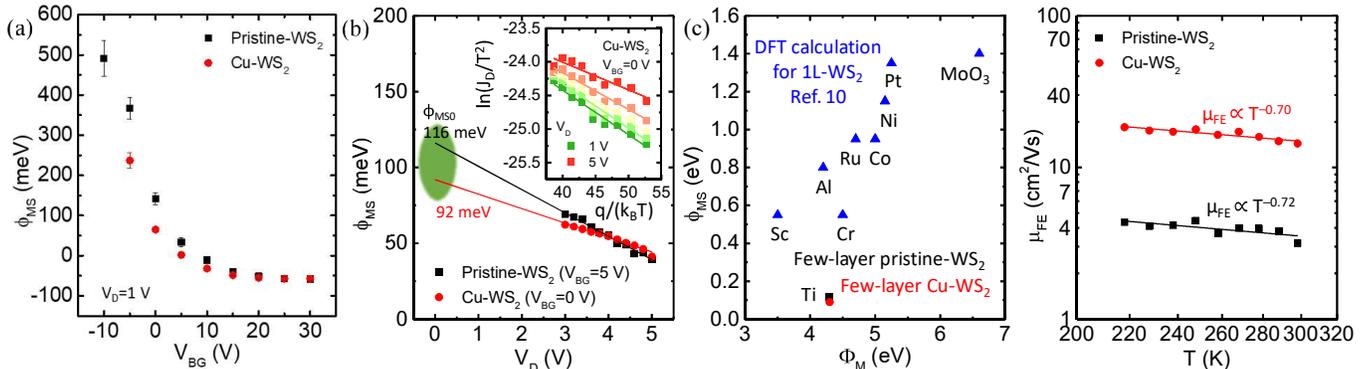

Fig. 8. (a) ϕ_{MS} as a function of V_{BG} for extracting ϕ_{MS0} at V_{FB}. (b) ϕ_{MS0} as a function of V_D for eliminating barrier lowering at finite V_D. (c) Comparison of ϕ_{MS} for various metal workfunctions (Φ_M).

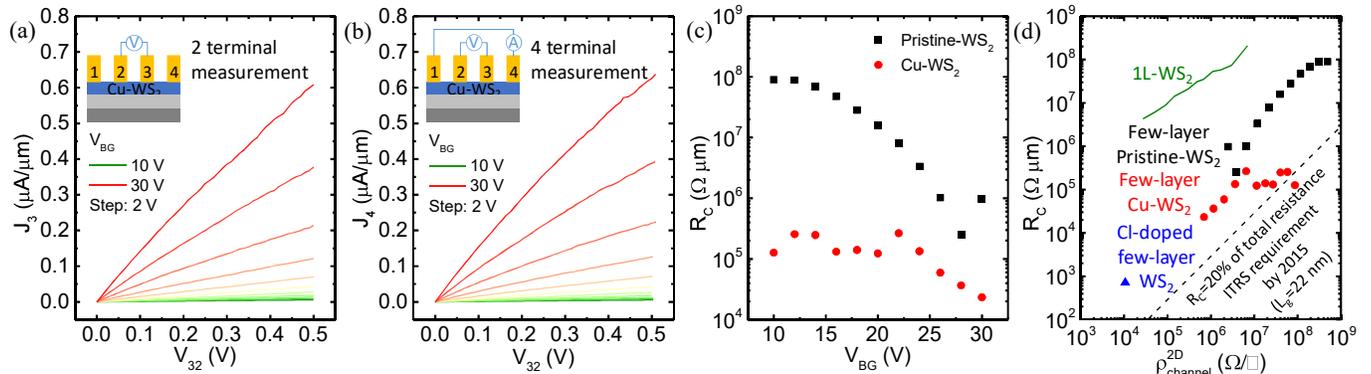Fig. 9. μ_{FE} as a function of T fitted by a power-law relation.

Fig. 10. (a) I-V relation of Cu-WS$_2$ FET in 2 terminal measurement. (b) I-V relation of Cu-WS2 FET in 4 terminal measurement. (c) Calculated R_c as a function of V_{BG}. (d) R_c as a function of $\rho^{2D}_{channel}$ for 1L-WS$_2$, few-layer WS$_2$ and chemically doped WS$_2$.
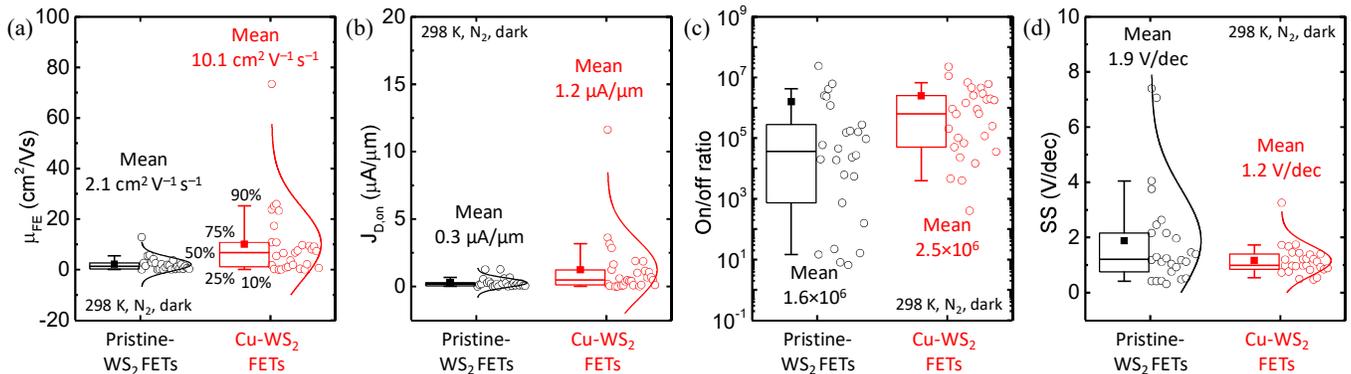

Fig. 11. A statistical study of transistor performance comparison for 26 pristine-WS$_2$ FETs and 29 Cu-WS$_2$ FETs, including (a) μ_{FE}, (b) on/off ratios, (c) $J_{D,on}$, and (d) SS.