Space-resolved controllable insulator-metal transition for rewritable grating

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Abstract

Doping is an effective way to tune the property of metal oxides\textsuperscript{1-5}, for achieving functional oxide electronics\textsuperscript{6-8}. Previously we developed a controllable hydrogen doping technology at ambient conditions by use of electron-proton synergistic doping strategy, which enables one to get rid of high-temperature/pressure treatments required by traditional technologies\textsuperscript{9}. Here, based on this facile doping route, we achieve a visual and reversible insulator-metal transition (MIT) for tungsten trioxide (WO\textsubscript{3}) film. Its outstanding spatial selection is comparable to standard UV lithography, which shows the potential of becoming a viable way for rewritable WO\textsubscript{3} grating device fabrication. Furthermore, the period of the obtained WO\textsubscript{3} structural grating can also be easily changed for requirement by doping area selection. This advanced doping technology opens up alternative approaches for developing not only optical devices, but also rewritable ions devices and integrated circuits for various oxide electronics.
Introduction

Atomic doping is an effective way to tune the properties of materials and fabricate functional electronic devices\textsuperscript{10,11}. It is well established that the silicon based semiconductor industry which has energized modern information technologies in digital era relies on the p-type or n-type silicon doping technology\textsuperscript{12,13}. Yet this doping technology requires extreme conditions such as high vacuum, high energy or high temperature for ion implantations\textsuperscript{14-16}. Hydrogenation for oxide material is an effective way to realize the electron doping as well as modulation the properties\textsuperscript{8,17,18}. For example, the H-doped TiO\textsubscript{2} particle, or the so-called black TiO\textsubscript{2}, showed the enhanced visible and infrared absorption for solar energy or photocatalysis applications\textsuperscript{19}. The hydrogenated VO\textsubscript{2} material show special continuous metal-insulator phase transitions depending on the H-doping concentration\textsuperscript{20}. While these reported hydrogenation in oxide materials were always achieved by direct H\textsuperscript{+} ions implantation or high temperature annealing in H\textsubscript{2} gas with noble metal catalysts.

The recently proposed doping method based on electron-proton synergistic effect is viable in ambient condition\textsuperscript{9}. It utilized separated electron and proton sources at room temperature, supplying a low-energy scale environment for the operation. In addition, the doped hydrogen atoms in oxide material can be driven out upon suitable temerperature annealing, making the facile electron doping process reversible and controllable. With this facile doping strategy, various oxide materials’ properties can be modulated and lots of applications are expected\textsuperscript{21}.

In this work, tungsten trioxide (WO\textsubscript{3}), a well-known electrochromic oxide material\textsuperscript{22-24}, was selected as an ideal platform for visible phase modulation by the electron-proton synergistic effect. After preparing a thin WO\textsubscript{3} film, we contacted it with a small Zinc particle and immersed them in a diluted acid solution. Then the film was smoothly hydrogenated and the H-doped induced insulator-metal phase transition was observed directly by eyesight due to the pronounced electrochromic effect. Combined with the standard UV lithography, the selective electron-doping area can be achieved, which was applied for the tunable grating devices. More importantly, the grating tripes
can be erased by high-temperature annealing in the air, making the devices controllable and reusable. Our experiment not only visualized the controllable insulator-metal transition in WO₃ film, but also demonstrated a facile and cost-effective way for rewritable grating devices or integrated circuits for various oxide electronics in the future.

**Results and Discussion**

**Fig 1a** shows a schematic diagram of electron-proton synergistic doping route. When an oxide semiconductor contacted with a proper metal particle are immersed into an acid solution, the electrons supplied by metal (yellow particle) and the free

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**Fig.1 | The electron-proton synergistic doping for WO₃ film.**

*a,* The schematic diagram of electron-proton synergistic doping route. The whole system is immersed into an acid solution. The purple bubbles are free protons and the yellow column is a low-workfunction metal particle.  
*b,* The mechanism of electron-proton synergistic doping effect: electrons flowing from metal with a higher Fermi level (i.e., lower workfunction $W_m$) to semiconductor with a lower Fermi level (i.e., higher workfunction $W_s$) at the interface.  
*c,* The workfunction values for Zn and WO₃.  
*d,* Experiments prove that Zn and WO₃ can realize the synergistic effect, which can be observed by eyesight due to the electrochromic effect.  
*e,* Schematic depiction: this synergistic effect has a good spatial selection.  
*f,* Sharp zinc pen was used to write “WO₃” on WO₃ film in acid solution.  
*g,* This synergistic effect is reversible by 300°C annealing in air.
protons in acid solution can be doped into semiconductor rather than the oxide being corroded by acid. This electron-proton synergistic effect was firstly reported in our previous work\textsuperscript{9}, which was due to the variation of Fermi level (\(E_F\)) between the semiconductor and metal as shown in Fig 1b. When the \(E_F\) level of metal was lower than that of semiconductor, the electrons in metal would flow into semiconductor for balancing their \(E_F\) levels. The interfacial charge transfer will not be continued due to the electrostatic screen effect. While if this metal/semiconductor contact was put into acid solution, the free protons in the solution would be attracted into semiconductor, forming the H-doped semiconductor layer. In addition, the protons insertion into semiconductor would metallize the contact area and break the electrostatic screen effect, which drove continuous electron doping into the semiconductor. The more detailed discussion was available in Fig S1.

Here, we noticed that WO\(_3\) could be a good sample due to its high work function\textsuperscript{25-27}, 6.59 eV, as shown in the histogram of Fig 1c. Indeed, when a WO\(_3\) film was touched by a zinc particle (~2 mm size) with the work function of 4.33 eV and put into a diluted H\(_2\)SO\(_4\) solution, a dark blue region was formed and spread quickly to the whole film in Fig 1d. An animated process is in Supplementary Video 1. Because the spreading speed is limited, the doping region can be controlled and selected easily as shown in the scheme of Fig 1e. In Fig 1f, a Zinc pen was used for writing the characters of “WO\(_3\)” in a piece of WO\(_3\) film. See more details in Fig S2 and Supplementary Video 2. More importantly, this electron doping in WO\(_3\) film is reversible. The “WO\(_3\)” characters were erased by 300°C annealing in air as shown in Fig 1g. The animated process is in Supplementary Video 3.

The H atoms existed in the samples were examined by secondary ion mass spectrum (SIMS) in Fig 2a. The results showed that after the metal-acid treatment, the WO\(_3\) film was hydrogenated into HxWO\(_3\) effectively, which had the highest H concentration (red curve) compared with the pristine WO\(_3\) (hyacinth curve) and restored WO\(_3\) (green curve). In contrast, O element was pretty constant for these three samples in Fig S3, thus the possible oxygen vacancies was excluded. It was reported that for many H doped insulators, their pristine characteristic peaks in Raman spectrum were
Fig. 2 | The characterizations for electron doping WO$_3$ film. a. The secondary ion mass spectrum (SIMS) tests for the WO$_3$ film after treated by electron-proton synergistic doping route, labeled by HxWO$_3$. Then the HxWO$_3$ annealed at 300℃ in air leads to the restored WO$_3$ sample. b. The Raman peak at 802 cm$^{-1}$ for pristine WO$_3$ film is disappeared in HxWO$_3$. While it can be restored after annealing the HxWO$_3$ sample. c. The UV-Vis-infrared transmission curves for the pristine WO$_3$, the HxWO$_3$ and the restored WO$_3$ samples. d. Resistance-Temperature (R-T) results show the resistance of pristine WO$_3$ film is quite stable within the temperature from 40 to 100 degrees, while it will decrease with six orders of magnitudes after the film was hydrogenated to HxWO$_3$, indicating a pronounced metal-insulator transition (MIT). The inset shows the R-T cycle test in air, showing the metallic HxWO$_3$ is quite stable at ambient. To verify this hint, we conducted UV-Vis-infrared transmission tests. Indeed, the great difference of the transmission for these three samples were observed in Fig 2c. The pristine WO$_3$ film showed very high visible and near-infrared transmission, while the transmission of the hydrogenated HxWO$_3$ film was close to zero, except the low transmission in the range from 350 nm to 530 nm. This transmission property was quite usually changed, even disappeared because of the hydrogenation$^{19,28,29}$. In Fig 2b, it was observed that the 802 cm$^{-1}$ peak for pristine WO$_3$ film was really disappeared for HxWO$_3$ film$^{30}$. Even the peaks of the sapphire substrate cannot be distinguished which may due to that the applied 633 nm excitation laser cannot go through the HxWO$_3$ film.
consistent with the observation in Fig 1d, which showed that the HxWO₃ film was heavily dark blue by eyesight.

As we know, infrared is usually reflected by metal, which implies a metal-insulator transition (MIT) between pristine WO₃ and HxWO₃. A more conviced electric characterization was conducted. Fig 2d showed the Resistance-Temperature (R-T) measurement for the pristine WO₃ film and the hydrogenated one. The resistance of pristine WO₃ film (~10⁸ Ω) was decreased up to 6 orders of maganitudes if hydrogenated to HxWO₃ (~10² Ω), indicating a pronounced MIT. It also pointed out that the metallic HxWO₃ was quite stable at ambient according to the R-T cycle tests in the inset of Fig 2d, which indicated the resistance of the HxWO₃ film showed little changes even heated up to 100°C. In addition, there was no noticeable variation in the scan electron microscope (SEM) results for the surface and cross-section scans for these film samples (Fig S4). Furthermore, from the X-ray diffraction (XRD) results, it was observed that there three films were all amorphous (Fig S5), since there were no related diffraction peaks for WO₃ in the curves, see more details in Experimental section.

The mechanism of the quick insertion of H atom into WO₃ film by the zinc-acid treatment was also investigated by theoretical calculations. Considering the Fermi level difference for the Zn/WO₃ interface, electrons would flow from Zn to WO₃. The computed differential charge distributions of Zn/WO₃ interface confirmed the charge transfer behavior (Fig 3a). Bader charge analysis found ~0.07 electrons being transferred from each Zn atom to WO₃, leaving negative charges in the WO₃ part. The extra negative charges in WO₃ (donated from Zn metals) would attract the surrounding protons in acid solution to penetrate into the semiconductor lattice. By simulating the reaction pathways of a Hydrogen atom migrating from WO₃ surface to subsurface (Fig S6), we demonstrated that the H-migration barrier (ΔE_b) is substantially lowered by increasing the number of negative charges (Fig 3b). With charge conditions of 1 hole, neutral, and 0.5 electron, the ΔE_b value is 2.46 eV, 1.32 eV and 1.20 eV, respectively. One can thus infer that electrons accumulated in the WO₃ can help proton diffusion into the lattice, and the meet of protons and electrons inside the lattice completes the hydrogenation of WO₃ semiconductor. Importantly, H-doping induces significant
changes to the electronic structures of WO$_3$. The calculated density of states (DOS) in Fig 3c-d show that the hydrogenation effective shifts up the Fermi level, closing the

![Diagram](image_url)

Fig.3 | Theoretical calculations for the hydrogenated WO$_3$. a. Computed differential charge distribution at Zn/WO$_3$ interface. Isosurface is 0.005 electrons per Å$^3$. b Energy diagram along the reaction pathways of H migrating from WO$_3$ surface (initial state: IS) to subsurface (final state: FS) via the transition state (TS). Energy of IS is set as zero. Density of states (DOS) of c WO$_3$ and d H-doped WO$_3$, together with inset photographs for the atomic models.

The original band-gap in WO$_3$ and consequently bestowing metallic features to the doped system of HxWO$_3$, which are responsible for the MIT and low transmissivity of visible light and infrared in our experiments.

Because the observed synergistic doping effect in diluted acide solution for WO$_3$ film is quite fast and the doping area is selective, some interesting patterns can be fabricated if combined with UV lithography method since photoresist is usually made by photopolymer materials$^{32}$, which are often stable in acid. In addition, the intrinsic WO$_3$ film and the HxWO$_3$ film showed very large resistance change (up to 10$^6$
difference) and pronounced transmission variation in visible and near-infrared range, optical grating device is possibly produced. Thus at first, we prepared a “big” pattern

**Fig.4** The performance of rewritable WO$_3$ grating device. **a**, Photoresist is covered on a WO$_3$ film as the shape of “USTC”, which proves that photoresist would hinder the electron-proton synergistic doping. **b**, The synergistic effect is compatible with standard UV lithography, which can be limited by photoresist to conduct in microchannels. **c-d**, The photos recorded by optical microscope: a photoresist array in a bar shape **(c)** and a photoresist array in a square shape **(d)**. After being processed by synergistic doping and lift-off, the corresponding pattern of bars **e** and squares **f** were obtained. For figures **c-f**, scale bar is the same. The period is 16 μm. **g-j** show the corresponding surface morphology of samples in figures **c-f**. **k-n**, the corresponding diffraction spots of samples in figures **c-f**. **o**, The structural grating of WO$_3$ in the period of 16 μm. **p**, surface morphology, **t**, diffraction spots. **q-s**, adjusting the period of the structural grating by the synergistic doping, 32 μm for figure **q**, 64 μm for figure **r**, 64 μm for figure **s**. **u-w** the corresponding diffraction spots of samples in figures **q-s**. For figures **o** and **q-s**, scale bar is the same. For figures **t-w** scale bar is the same.
on a WO$_3$ film as the shape of “USTC” by a photoresist layer. It was found that the covered parts (the four characters) kept the original WO$_3$ phase, while the other areas were all hydrogenated, showing the fact that the photoresist layer can hinder the synergistic effect (Fig 4a and Supplementary Video 4). Furthermore, by UV lithography, a set of bars covered with photoresist were fabricated in Fig 4b. Then the bare microchannels of WO$_3$ film can be “dyed” freely by moving and touching a Zn probe in acid, for example, the two microchannels were selected to be hydrogenated. A demonstration is in Supplementary Video 5.

Based on the above results, it was suggested that a tunable and controllable optical grating device could be produced in this way. A bar array and a square array of photoresist were fabricated by standard UV lithography on two WO$_3$ films in Fig 4c and Fig 4d, respectively. The period was 16 μm for the bar array in the horizontal direction and for the square array in both horizontal and perpendicular directions. Fig 4g and Fig 4h show surface morphology of these two arrays respectively by a three-dimensional profilometer. The thickness of the covered photoresist layer on each line or each square was more than 2 μm. Actually, these periodic arrays were structural grating proved by diffraction measurement (setup of the probe device is in Fig S7), two sets of spot appearing in Fig 4k and Fig 4l were observed respectively.

While if treat these two arrays by metal-acid route, the areas with no photoresist layer were hydronagted to metallic state as shown in Fig S8. After lift-off, the pattern of bars and squares were made in WO$_3$ films as shown in Fig 4e and Fig 4f, respectively (expanded results in Fig S9). The contrast of the patterns should be originated from the difference of metal and insulator areas. The diffraction spots patterns were recored in Fig 4m and Fig 4n, and quite consistent with those in Fig 4k and Fig 4l from the grating with covered photoresist layer. This results indicate our synergistic effect was an outstanding technology for grating fabrication. In addition, we should emphasize that this kind of grating is different from the common structural grating such as shown in Fig 4c and Fig 4d with grooves, because these novel gratings are composed by the periodic metal and insulator WO$_3$ area with quite smooth surface (Fig 4i and Fig 4j). More importantly, this kind of optical grating can be restored and reprocessed, since
these periodic patterns could be removed by 300°C annealing in air, then the diffraction spots were disappeared as shown in Fig S10.

Another advantage for optical grating fabrication in this way was that the period of structural grating was tunable and selective. By combining UV lithography and reactive ion etching (RIE), a WO$_3$ structural grating of 16 μm period was made in Fig 4o with the surface morphology of Fig 4p and the related diffraction spots in Fig 4t. We put this grating device in dilute H$_2$SO$_4$ solution. Then the original period could be easily doubled to be 32 μm by a Zn probe contacting the WO$_3$ bars alternatively, since the touched WO$_3$ bars were hydrogenated and“dyed” quickly. Resultantly, the period of diffraction spots is half of the original period as shown in Fig 4u. While if only a quarter of WO$_3$ bars was “dyed” (Fig 4r), which means a new period of 64 μm, the period of diffraction spots is 1/4 of the original one (Fig 4v). These results are consistent with the reciprocal law of grating diffraction$^{33}$. To further verify the observation, another way to realize the grating period of 64 μm, dyeing three quarters of WO$_3$ bars, was also conducted in Fig 4s. Indeed, the diffraction spots in Fig 4w are the same as that in Fig 4v. The expanded photos of the gratings in different periods are in Fig S11, indicating the flexible period selection of grating device by the current synergistic doping way in acid solution. More importantly, it should be emphasized again that all the processed gratings can be restored by annealing as shown in Fig S12, making this technique suitable for rewritable grating device fabrication in the future.

**Conclusion**

To conclude, we applied electron-proton synergistic doping process to WO$_3$ film successfully and realized a direct visualization of insulator-metal transition in WO$_3$ film due to its pronounced electrochromic effect. This phase transition is originated from the H atoms doping, which results in a stable metallic state of WO$_3$ film in the air. Combined with the standard UV lithography technique, we developed an advanced technology for fabrication a flat WO$_3$ grating device. In addition, the period of the structural WO$_3$ grating can be tuned by selective hydrogenation. More importantly, all
the prepared gratings can be restored via an annealing procedure and reused. Our experiment not only demonstrate a facile electron-proton synergistic doping stragey for oxide material, but also supply a technique for tunable and rewriterable grating device fabrication in the future.

**Experimental Section**

**WO₃ film deposition**

WO₃ thin films were prepared on c-Al₂O₃ single-crystal substrates by reactive magnetron sputtering in an argon–oxygen atmosphere at 200°C with a stoichiometry WO₃ target. Before loading the Al₂O₃ substrates into the chamber, they were cleaned with acetone and ethanol in an ultrasonic bath and then rinsed several times with de-ionized water. The flow rates of argon and oxygen were fixed at 60.0 and 1.0 SCCM, respectively. The radio-frequency sputtering power during the deposition was maintained at 80 W. Under these conditions, the prepared WO₃ thin films were amorphous. The amorphous structure is in favor of the ions/protons insertion into WO₃ film and induced quick electrochromic results.³⁴,³⁵ The final thickness of the prepared film was ~260 nm.

**Characterizations**

The purity of Zinc particle and needle is >99.99%. The 2%wt H₂SO₄ solution was adopted in all experiments. The square resistance as a function of temperature was examined by an electric measurement system (ZJ2810B) with a variable temperature stage (Eurotherm 3504). The average rate of heating up is 0.15 K/s and cool down by nature. High sensitive secondary-ion mass spectrometry (SIMS) measurements (Quad PHI6600) were conducted to directly examine the hydrogen, oxygen, aluminum concentration in each sample. To examine the crystal structure, XRD tests were carried out by Philips X’pert Pro, radiation source Cu Kα, λ = 0.15148 nm. The SEM images were recorded by XL-30 ESEM. Raman spectroscopy tests were recorded at room temperature by LabRAM HR Evolution. A 633 nm laser was used as the excitation
source. The optical transmission was measured at room temperature by using a UV–Vis–IR spectroscopy (SolidSpec 3700). A home-made device was used for measuring the diffraction of the grating. The wavelength of the laser is 532 ± 10 nm. The max output power is less than 3000 mW. A three-dimensional profilometer (ContourGT-K 3D Optical Microscope) was used to measure surface morphology. An optical microscope (Leica DM8000) was used to record microimages. Photoresist arrays were made by standard UV photolithography. Reactive ion etching (RIE) was conducted by Oxford, Plasma Pro NGP 80.

**Computational details**

All the calculations of the present work were performed by the Vienna Ab Initio Simulation Package (VASP) with the density functional theory (DFT). We chose the frozen-core all-electron projector augmented wave (PAW) model for core states and the Perdew–Burke–Ernzerh (PBE) for exchange and correlation functional. We set the kinetic energy cutoff of 400 eV for the plane-wave expansion of the electronic wave function. We set the force and energy convergence criterion to be 0.02 eV/Å and 10–5 eV, respectively. The length of vacuum space was 20 Å to avoid interactions between periodic images. The solid-solid interfaces is built by attaching the Zn and WO₃ surface with mismatch below 5%. The energy barrier was calculated as \(\Delta E_b = E_{TS} - E_{IS}\), where \(E_{TS}\) and \(E_{IS}\) represent the energies of the initial structures (IS) and the transition states (TS). The energy calculations of present work were corrected by zero-point energy.

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**Author contributions**

Y.C. and C.Z. conceived the project. Y.C. fabricated the devices, performed the measurements and analyzed the data. C.H., X.Z. and B.L. grew the WO₃ films. C.H. performed the SEM, XRD, and Raman characterizations. L.X. and J.J. conducted the theoretical calculations. Y.C. and C.Z. wrote the paper and all authors commented on it.

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