Suppression of Metal-Insulator Transition in VO₂ by Electric Field–Induced Oxygen Vacancy Formation

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Electrolyte gating with ionic liquids is a powerful tool for inducing novel conducting phases in correlated insulators. An archetypal correlated material is vanadium dioxide (VO₂), which is insulating only at temperatures below a characteristic phase transition temperature. We show that electrolyte gating of epitaxial thin films of VO₂ suppresses the metal-to-insulator transition and stabilizes the metallic phase to temperatures below 5 kelvin, even after the ionic liquid is completely removed. We found that electrolyte gating of VO₂ leads not to electrostatically induced carriers but instead to the electric field—induced creation of oxygen vacancies, with consequent migration of oxygen from the oxide film into the ionic liquid. This mechanism should be taken into account in the interpretation of ionic liquid gating experiments.

he electric field-induced metallization of correlated insulators is a powerful means of creating novel electronic phases, but the process requires high electric fields often beyond those achievable by conventional dielectric gates (1-3). Such fields can be achieved at interfaces with the use of Schottky junctions (4) or polar materials (5, 6), or at surfaces with the use of ionic liquids (ILs) (7) as the gate dielectric in field-effect transistor devices (8-10). The latter method allows for tunable electric fields without restriction on the channel material or its crystal orientation. One of the most interesting and widely studied correlated materials is the insulator VO_2 (11, 12), which exhibits a metal-to-insulator phase transition (MIT) as the temperature is reduced below ~340 K in bulk material (13). Recently, electrolyte gating (EG) was shown to substantially alter the properties of thin films of VO₂; in particular, the metallization of the insulating state was achieved and attributed to the introduction of small numbers of carriers that are electrostatically induced by the gating process (14). This would be consistent with the destabilization of a Mott insulating state in VO₂ that depends critically on electronic band halffilling, which has been a long-standing goal in condensed matter physics (15). We find that an entirely different mechanism accounts for the EG suppression of the MIT to low temperatures in epitaxial thin films of VO2 that we have prepared on TiO₂ and Al₂O₃ single-crystal substrates.

Figure 1A shows resistivity-temperature curves for VO₂ films grown by pulsed laser deposition on various facets of TiO₂ and Al₂O₃ single crystals in an O₂ pressure (P_{O_2}) of 10⁻² torr during deposition (*16*). The MIT temperature (T_{MIT}) varied as a result of different strains in the VO₂ films (17). Henceforth, we focus on films grown on TiO₂(001) and Al₂O₃(1010), which have a large difference in $T_{\rm MIT}$ but have the same crystallographic orientation. For these films, highresolution x-ray diffraction (Fig. 1B) indicated excellent epitaxial growth with the *c* axis out of the plane. The film on TiO₂(001) is 10 nm thick, is strained along the *c* axis by -1.2% (18, 19), and has a T_{MIT} of ~290 K. By contrast, the film on Al₂O₃(1010) is 20 nm thick, is completely relaxed (*18*, *19*), and has a T_{MIT} of ~340 K.

Devices for EG studies were fabricated from 10-nm VO₂/TiO₂(001) and 20-nm VO₂/Al₂O₃(1010) films (Fig. 1C), unless otherwise noted, using standard optical lithographic techniques. The electrical contacts to the channel included source and drain contacts as well as four side contacts that were used for four-wire resistance and Hall measurements. A ~100-nl droplet of the IL 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (HMIM-TFSI) covered the channel and lateral gate electrode. The gate voltage $V_{\rm G}$ was swept at 5 mV/s and a source drain voltage V_{SD} = 0.1 V was used, except where noted. Hysteresis in the sheet conductance centered about $V_{\rm G} = 0 \, {\rm V}$ was observed for both substrates (Fig. 1, D and E). By sweeping $V_{\rm G}$, the device could be reversibly switched between low- and high-conductance states. Once switched to the high-conductance state, the device was stable at $V_{\rm G} = 0$ V and maintained its conductance for many days, even when the IL was washed off the device with isopropyl alcohol (fig. S1). We used x-ray photoelectron spectroscopy (XPS) to verify that the IL was completely removed; no spectroscopic signature of the IL was found (fig. S2). This suggests that the gating effect was not electrostatic in



Fig. 1. Temperature- and gate voltage–dependent conductivity of epitaxial VO₂ thin films. (**A**) Resistivitytemperature curves for VO₂ films grown on various orientations of TiO₂ and Al₂O₃ single–crystal substrates. (**B**) High-resolution Cu K α θ -2 θ x-ray diffraction pattern of VO₂ films deposited on Al₂O₃(1010) and TiO₂(001), respectively, showing highly oriented films with the *c* axis out of plane. (**C**) Optical image of a typical device showing a droplet of the ionic liquid (IL) HMIM-TFSI. The electrical contacts can be seen in the magnified image of the channel (right). S, source contact; D, drain contact; G, gate electrode. (**D** and **E**) Sheet conductance versus V_G for devices fabricated from VO₂ films prepared on Al₂O₃(1010) (D) and TiO₂(001) (E).

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origin. Moreover, the fact that films on both types of substrates showed similar behavior rules out any appreciable influence of the substrate—for example, the role of strain. The electric field induced metallic phase, reflected in the sourcedrain current $I_{\rm SD}$, was stable over extended periods

Fig. 2. Suppression of the MIT in VO₂ films. (A) Sheet resistance R_s versus temperature T for various gate voltages varying from 0 to 1.8 V for VO₂/TiO₂(001). (B) Resistivity of VO₂ versus temperature as a function of P_{0_2} used for film deposition on TiO₂(001). (C) R_s versus T for the same device as in (A) in its pristine state, at $V_{\rm G} = 1.8$ V (gated) and at $V_{\rm G} = -0.8$ V (reverse gated), showing complete recovery of the MIT in the latter case. V_G was applied at 300 K for measurements in (A) and (C) while the films were in their metallic state. (D) Sheet resistance for EG devices formed from VO₂/TiO₂(001) and $VO_2/Al_2O_3(10\overline{1}0)$, and electron carrier density ne from Hall measurements for an EG device fabricated from $VO_2/TiO_2(001)$, versus V_G . The dashed line is a guide to the eye.

Fig. 3. XPS and SIMS measurements. (A and B) V 2p core-level spectra for pristine and gated $VO_2/TiO_2(001)$ (A) and $VO_2/Al_2O_3(10\overline{1}0)$ (B); $V_G =$ 1.8 V in both cases. (C) Comparison of data in (A) and (B) with spectra for VO₂ films deposited under reduced P_{0_2} on TiO₂(001). (D) Excess ¹⁸O concentration above the natural abundance (~0.2 atomic %) versus depth for two EG devices fabricated from 40- and 20-nm VO₂ on Al₂O₃(1010) determined by SIMS. The devices were gated to the metallic state in vacuum and reverse-gated to recover the insulating state in ¹⁸O₂. Data are compared to pristine channels on the same wafer that were not gated but were subjected to the same dosage of ¹⁸O₂. Measurements on two different areas of sample 1 are very similar. (E) Scan at a mass resolution of 4000 (atomic mass units divided by full width at half maximum) showing clear separation of ${}^{18}O$, ${}^{16}O^{1}H_{2}$, and ${}^{17}O^{1}H$.

of time in the presence of the IL at $V_G = 0$ V (fig. S3A) and also for modest V_G , but the insulating phase could be nearly recovered by applying reverse gate voltages similar in value to those needed to induce the metallic phase (Fig. 1, D and E). The insulating phase could also be recovered by

annealing in oxygen at modest temperatures (~200°C; fig. S4).

Figure 2A shows the temperature dependence of the channel sheet resistance $R_{\rm S}$ of VO₂/TiO₂(001) devices for several positive values of $V_{\rm G}$. A progressive suppression of the MIT as the gate bias



was increased is observed until the MIT is suppressed to below 5 K at $V_{\rm G} \sim 1.8$ V. This gating effect is compared in Fig. 2B with the effect of changing the oxygen content of VO₂ by depositing VO₂/TiO₂(001) in reduced P_{O_2} at 400°C. The T_{MIT} is systematically reduced and the MIT is suppressed as P_{O_2} is lowered. The transport data in Fig. 2, A and B, are notably similar. In both cases, the onset temperature for the MIT is decreased and the magnitude of the resistivity change drops. The similarity in these data suggests that the EG effect could also be due to the electric field-induced formation of oxygen vacancies, thereby leading to a reduced MIT.

As discussed above, the VO₂ devices can be reversibly switched between insulating and metallic phases. The temperature dependence of the resistivity for the same device in Fig. 2A in its pristine (i.e., ungated) state is nearly identical after being reversibly gated (Fig. 2C).

The sheet resistance in the metallic phase just above the MIT is plotted versus $V_{\rm G}$ in Fig. 2D for the devices used in Fig. 2A, and for devices on Al₂O₃ substrates in fig. S5. For VO₂ devices on both substrates, $R_{\rm S}$ increases considerably as $V_{\rm G}$ is increased. If the gating effect were electrostatic, the electron carrier density $n_{\rm e}$ should increase for positive $V_{\rm G}$; thus, one would anticipate a decrease rather than an increase in $R_{\rm S}$. Moreover, Hall resistivity measurements for VO2/TiO2 show no evidence for any increase in n_e (Fig. 2D, bottom); rather, $n_{\rm e}$ is independent of $V_{\rm G}$ and its measured value is $\sim 6 \times 10^{22}$ cm⁻³, similar to bulk VO₂ (20).

To confirm the possibility of oxygen vacancy creation during EG that was suggested by our transport data, we carried out three independent experimental studies. First, we used XPS to measure changes in the oxidation state of vanadium in gated VO₂ films. Devices with much larger channel areas (~900 by 300 µm) than those used above were fabricated to accommodate the x-ray (Al K α) beam size (diameter ~150 μ m). Transport data for these devices were similar to those shown in Fig. 2 for similar $V_{\rm G}$. In Fig. 3, A and B, the V 2p core-level spectra obtained within the channel for pristine devices are compared with the spectra for the same devices gated to completely suppress the MIT to low temperatures. The results for devices fabricated on $Al_2O_3(10\overline{1}0)$ and $TiO_2(001)$ are similar. The position of the V $2p_{3/2}$ core-level peak in the pristine sample is ~516.3 eV, close to the well-established value of ~516.1 eV for V^{4+} in VO₂. In the gated sample (for which the IL was removed), the V 2p3/2 core-level peak broadens and is shifted toward lower binding energy by ~0.2 eV. (Note that the peak is observed to be at ~515.8 eV for V^{3+} in V_2O_3 .) These observations indicate a reduction in the oxidation state of V from V⁴⁺ toward $V^{3+}(21)$. Similarly, in situ measured films prepared at different values of $P_{\Omega_{\alpha}}$ (Fig. 3C) have V 2p peaks that shift systematically to lower binding energies and broaden monotonically as P_{O_2} is reduced. Thus, the Voxidation state con-tinuously evolves toward V³⁺, concomitant with a suppression of the MIT (as shown in Fig. 2B).

The changes in the oxidation state of V observed by XPS strongly indicate the formation of oxygen vacancies. In the absence of electric fields, the formation energies of oxygen vacancies in rutile oxides are known to be very high (22). However, we hypothesize that the electric fields created at the electric double layer (EDL) at the IL-oxide interface are sufficiently high (23) to drive oxygen out of the VO2 surface into the IL, and that once the oxygen vacancies are created, these vacancies are stable in the absence of the EDL at $V_{\rm G} = 0$. This explains the nonvolatility of the gating (Fig. 1, D and E). To test this hypothesis, we carried out gating in a high-vacuum chamber in which we could introduce ¹⁸O₂. First, an EG device with a large channel area (900 by 300 μ m) was gated in high vacuum ($V_{\rm G} = 3$ V) to suppress the MIT to low temperatures. After gating for long times (~10 to 20 min), the channel conductance was found to be nearly saturated and remained unchanged when VG was reduced to zero (16). Once a stable channel current was obtained, ¹⁸O₂ was introduced into the chamber at $V_{\rm G} = 0$ V. Then a reverse gate voltage of -1.5 V was applied until the insulating state was recovered; this took several hours. This proce-



Fig. 4. Electrolyte gating of a device fabricated from VO₂/Al₂O₃(1010) in the presence of oxygen at 300 K. (A) Source-drain current at $V_{\rm G}$ = 3 V versus time as $P_{\rm O_2}$ was varied from an initial pressure of 150 torr, gradually reduced to 10⁻⁵ torr, abruptly increased to 130 torr, and then gradually reduced to 10⁻⁵ torr (indicated schematically by color). (B) Sheet conductance (color scale) as a function of $V_{\rm G}$ and $P_{\rm O_2}$.

dure was repeated three and four times, respectively, for two experimental devices termed sample 1 and sample 2. Samples 1 and 2 were fabricated from 40-nm and 20-nm $VO_2/Al_2O_3(10\overline{1}0)$, respectively. Depth profile secondary ion mass spectrometry (SIMS) was then performed on these devices after the IL was removed. A comparison was made to pristine regions on the same sample that were otherwise subjected to identical procedures concurrently. In the latter case, no excess ¹⁸O above its natural isotopic abundance in oxygen (0.2 atomic percent) was measured. However, a notable increase in the concentration of ¹⁸O to nearly twice the natural abundance was found at the surfaces of both devices in the gated channels, with a higher value in sample 1, the device that was gated in higher pressures of ¹⁸O₂ (Fig. 3D). The excess ¹⁸O was seen to depths of nearly 20 nm from the oxide surface, with similar depth profiles for the two samples. The incorporation of ¹⁸O within the VO₂ channels during reverse gating supports our hypothesis that gating creates oxygen vacancies within the channel.

Given the large area of the channel, the most likely migration path for the oxygen that must be released to create the vacancies during gating is into the IL. Then one might speculate that saturation of the IL with oxygen would prevent such migration. Figure 4A indeed shows that there is no change in the source-drain current even when a large $V_{\rm G}$ is applied in the presence of O₂ (at 150 torr) to a 100 by 20 µm device of $VO_2/Al_2O_3(10\overline{1}0)$. After 200 s, O_2 was pumped out from the chamber and, concomitantly, ISD gradually increased. When oxygen was reintroduced into the chamber while maintaining $V_{\rm G} =$ 3 V, ISD began to decrease. We found a clear correlation between the source-drain current and the amount of oxygen in the chamber. A detailed dependence of the sheet conductance on $V_{\rm G}$ and P_{O_2} is shown in Fig. 4B. Appreciable gating effects were found only at low values of P_{O_2} (for $V_{\rm G} > \sim 1.5$ V).

Downloaded from https://www.science.org on January 28, Our experiments show that modest gate voltages result in the electric field-induced migration of oxygen into and out of the IL even though the energy required to create an oxygen vacancy in VO₂ in zero electric field is high. This phenomenon is likely to be common to many experiments using high electric fields, especially those using IL gating; many of these experimental results have been interpreted by the electrostatic creation of carriers. Our results suggest that the electric field-induced migration of species into and out of electrolyte-gated materials is an exciting avenue for the creation of novel, non-equilibrium phases of matter.

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Supplementary Materials

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Photonic Spin Hall Effect at Metasurfaces

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The spin Hall effect (SHE) of light is very weak because of the extremely small photon momentum and spin-orbit interaction. Here, we report a strong photonic SHE resulting in a measured large splitting of polarized light at metasurfaces. The rapidly varying phase discontinuities along a metasurface, breaking the axial symmetry of the system, enable the direct observation of large transverse motion of circularly polarized light, even at normal incidence. The strong spin-orbit interaction deviates the polarized light from the trajectory prescribed by the ordinary Fermat principle. Such a strong and broadband photonic SHE may provide a route for exploiting the spin and orbit angular momentum of light for information processing and communication.

he relativistic spin-orbit coupling of electrons results in intrinsic spin precessions and, therefore, spin polarization-dependent transverse currents, leading to the observation of the spin Hall effect (SHE) and the emerging field of spintronics (1-3). The coupling between an electron's spin degree of freedom and its orbital motion is similar to the coupling of the transverse electric and magnetic components of a propagating electromagnetic field (4). To conserve total angular momentum, an inhomogeneity of material's index of refraction can cause momentum transfer between the orbital and the spin angular momentum of light along its propagation trajectory, resulting in transverse splitting in polarizations. Such a photonic spin Hall effect (PSHE) was recently proposed theoretically to describe the spinorbit interaction, the geometric phase, and the precession of polarization in weakly inhomogeneous media, as well as the interfaces between homogenous media (5, 6).

However, the experimental observation of the SHE of light is challenging, because the amount of momentum that a photon carries and the spinorbit interaction between the photon and its medium are exceedingly small. The exploration of such a weak process relies on the accumulation of the effect through many multiple reflections (7) or ultrasensitive quantum weak measurements with pre- and postselections of spin states (8, 9). Moreover, the present theory of PSHE assumes

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the conservation of total angular momentum over the entire beam (5-9), which may not hold, especially when tailored wavelength-scale photonic structures are introduced. In this work, we demonstrate experimentally the strong interactions between the spin and the orbital angular momentum of light in a thin metasurface—a two-dimensional (2D) electromagnetic nanostructure with designed in-plane phase retardation at the wavelength scale. In such an optically thin material, the resonanceinduced anomalous "skew scattering" of light destroys the axial symmetry of the system that enables us to observe a giant PSHE, even at the normal incidence. In contrast, for interfaces between two homogeneous media, the spin-orbit coupling does not exist at normal incidence (5-9).

Metamaterial made of subwavelength composites has electromagnetic responses that largely originate from the designed structures rather than the constituent materials, leading to extraordinary properties including negative index of refraction (10, 11), superlens (12), and optical invisibilities (13, 14). As 2D metamaterials, metasurfaces have shown intriguing abilities in manifesting electromagnetic waves (15, 16). Recently, anomalous reflection and refraction at a metasurface has been reported (17, 18), and a variety of applications, such as flat lenses, have been explored (19-22). However, the general approach toward metasurfaces neglects the spin degree of freedom of light, which can be substantial in these materials. We show here that the rapidly varying in-plane phase retardation that is dependent on position along the metasurface introduces strong spin-orbit interactions, departing the light trajectory (S) from what is depicted by Fermat principles, $S = S_{\text{Fermat}} + S_{\text{SO}}$ (where S_{SO}



verse polarization splitting induced by a metasurface with a strong gradient of phase retardation along the *x* direction. The rapid phase retardation refracts light in a skewing direction and results in the PSHE. The strong spinorbit interaction within the optically thin material leads to the accumulation of circular components of the beam in the transverse directions (y' directions) of the beam, even when the incident angle is normal to the surface.

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Mind the Vacancies

Varying the carrier density of solid-state systems to manipulate their electrical properties usually involves chemical doping, which can lead to disorder. Recently, ionic liquids have been used to form an electronic double layer on the surface of a material, tuning its carrier density by the application of an electric field. Jeong *et al.* (p. 1402) used liquid gating on VO, which undergoes a metal-insulator transition close to room temperature. The liquid gating suppressed the transition to lower and lower temperatures; however, the material remained in the metallic state, even when the gating fluid was washed off. It appears that, instead of a simple electrostatic effect, the properties of VO are modulated by the introduction of oxygen vacancies, an electrochemical consequence of high electric fields. The results imply that careful interpretation of liquid gating experiments in condensed matter physics is needed.

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