Surface effects in metal oxide-based nanodevices

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As devices shrink to the nanoscale, surface-to-volume ratio increases and the surface–environment interaction becomes a major factor for affecting device performance. The variation of electronic properties, including the surface band bending, gas chemisorption or photodesorption, native surface defects, and surface roughness, is called "surface effects". Such effects are ambiguous because they can be either negative or beneficial effects, depending on the environmental conditions and device application. This review provides an introduction to the surface effects on different types of nanodevices, offering the solutions to respond to their benefits and negative effects and provides an outlook on further applications regarding the surface effect. This review is beneficial for designing nano-enabled photodetectors, harsh electronics, memories, sensors and transistors via surface engineering.

1. Introduction

Since the beginning of the 21st century, the scientific community has demonstrated many promising applications based on metal oxides due to their unique physical, chemical and optical properties. The distinct properties of metal oxides originate from the surface effects, including surface band bending (SBB), surface roughness, gas chemisorption, photodesorption, and surface related defects or states.1,2 Because metal oxides can be synthesized by a great variety of available deposition methods, complex shaped nanostructures are achievable.3–8 As the sizes decrease, the increase in surface area to volume ratio (S/V) makes the surface effect become more pronounced. From the electrical point of view, because the charge screening length (Debye length) is of the same order (∼100 nm) as that of the material thickness, altering the surface states could cause a dramatic change in electric

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properties. At the nanoscale level, the surface effect is ambiguous because it can act in either a detrimental or beneficial role depending on the application. Regarding the vulnerability of nanomaterials to the variance of the surroundings, such effects are usually detrimental in device-level applications. For example, a problem faced in an oxide transistor is that the interaction with ambient molecules and illuminating photons could cause degradation of device performance. In addition, the performance of resistive, switching-based devices could degrade with variation of environment conditions due to environment induced instability. On the other hand, facilitated by surface effects, the performance and sensitivities of nano-enabled sensors could be greatly improved. For example, nanostructures with a higher S/V ratio exhibit superior sensitivity in optical and chemical sensors compared to their thin film counterparts. Furthermore, surface modifications enable the electronic properties to be engineered at the nanoscale. Effective modifications could be achieved by chemical or physical approaches thereby helping to improve the sensitivity, detection selectivity, and stability of the devices. Surface modifications are not only important in metal oxide-based nanoscale devices but every class of nanoscale device such as organic thin-film transistors (OTFTs).

To develop the novel applications of nanostructures utilizing the surface effect, it is very important to understand how the physical properties are affected as the materials’ dimensions are reduced. In this study, we present the surface effect on metal oxide-based nanodevices, including photodetectors, harsh electronics, resistive random access memories, gas sensors and transistors. We highlight the benefits, discuss the major constraints arising from the detrimental consequences and provide a perspective outlook for future device applications.

2. Surface effect in different types of nanodevices

2.1. Applying the surface effect in nano-optoelectronics and eliminating the surface-induced instability for harsh electronics

Metal-oxide nanomaterials are promising in applications of photodetection and photovoltaics for their ultrahigh sensitivity and spectral selectivity. To the best of our knowledge, ultrahigh internal photogain of up to $10^8$ has been observed in ZnO nanowire (NW) devices. High photosensitivities are attributed to the presence of abundant deep-level states at metal oxides’ surfaces combining with a gas desorption/reabsorption process. In detail, the trap states at surfaces serve as the adsorption sites for gas molecules, namely O$_2$, to adsorb on the metal oxide surface and capture free electrons. The absorbed molecules act as acceptors, which reduce the carriers density and deplete the surface electronic states, leading to the formation of the space charge region and surface band bending (SBB). When illuminated by the light, the photo-generated electron–hole pairs are separated by the built-in potential formed by SBB, wherein the holes neutralize the O$^-$, which leads to a desorption process of the oxygen. Therefore, because the holes are “trapped” by the oxygen desorption/reabsorption process, the lifetime of the electrons is greatly prolonged, leading to the ultrahigh photogain.

Taking ZnO NWs as an example, the band bending is up to 1.5 eV and a few tens of nanometers in width (43 nm measured in air), determined by ultraviolet photoelectron spectroscopy (UPS) (Fig. 1a). A 100 °C heat treatment could cause a decrease of the SBB (from 1.5 eV to 0.74 eV and 43 nm to 30 nm) attributed to the removal of adsorbed oxygen molecules from the nanomaterial’s surfaces. On the other hand, decoration of Au nanoparticles (NPs) can enhance the SBB to 2.3 eV and 53 nm in width due to the creation of open-circuit nano-Schottky junctions and catalytically increase the amount of the O$_2$ adsorbates (Fig. 1b). Because the photon–electron

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conversion behaviours are dominated by the SBB, optoelectronic properties of metal oxides are tuneable through engineering of this trivially thin region near the surface.\(^{11,12}\) One simple way to control the optoelectronic properties is by engineering the size of the nanomaterials. For example, ZnO NW devices can be fully depleted or partially depleted, simply determined by the diameter of the NWs.\(^{11}\) By decreasing the diameter of NWs from 400 to 100 nm, the response speed increases from 31 to 5 s due to the diameter-dependent SBB. To engineer the surface effect, Chen et al. have shown that by decorating with Au NPs, the sensitivities of ZnO NW-based photodetectors can be enhanced due to enhancement of the surface effect.\(^{12,17}\) To further deplete the surfaces, Retamal et al. have recently demonstrated that n-type ZnO NWs decorated by p-type single-crystalline NiO NPs can produce a photogain of \(\sim 2.8 \times 10^8\), which is 3 orders of magnitude higher than that of pristine ZnO NWs (Fig. 1c).\(^{18}\)

However, as a side effect, high photogain metal-oxide devices normally suffer from the detrimental responsivity-speed trade-off owing to the slow adsorption/desorption process.\(^{16}\) This effect reduces the response speed to an unsatisfying value from several seconds to several hundreds of seconds. These faulty features limit their applications for various tasks and preclude the opportunities of metal-oxide nanodevices for real-time sensing. Some strategies have been proposed for the improvement of the response speed. From the electrical viewpoint, during light illumination, the generated electrons keep on accumulating, resulting in a rise of photocurrent until the equilibration of \(\text{O}_2\) desorption and readesorption processes. When turning off the light, holes recombine quickly with electrons, whereas there are still many electrons left in the metal oxide. It takes time for oxygen molecules to readsorb onto the surface and capture these electrons, leading to a slow recovery time. By fabricating the device with Schottky contacts, photon-electron couplings within materials can be facilitated and the response speed can be improved via the quick regulation of the Schottky barrier height.\(^{19,20}\) The use of one-Schottky-contact geometry reported by Zhou et al. demonstrates that both the sensitivity of a ZnO NW photodetector can be greatly promoted and the response time improved to 0.6 s.\(^{16}\) Multiple junctions can be formed by introducing a network scheme, which is an effective approach to improve recovery speed. For example, Chen et al. have shown that by fabricating the devices in a network manner, the response speed can be improved by 2 orders of magnitude compared to the single nanobelt (NB) devices (Fig. 2a and b).\(^{21,22}\) To maximize the Schottky contact, modification through a nanostructure design, for example, core–shell geo-

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**Fig. 1** Schematic of surface band bending for (a) oxygen-adsorbed NWs, (b) Au-decorated NWs and (c) NiO-decorated NWs.

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**Fig. 2** (a) Schematic of the ZnO NB networks photodetector. The inset is the top–view SEM image of the ZnO NBs on the prefabricated Ti/Au electrodes. (b) Comparison of the time-resolved photocurrents of the ZnO NB networks and a single ZnO NB under UV illumination. (c) A TEM image of a TiO\(_2\)-coated MWNT core–shell NW. (d) I–V characteristics of the TiO\(_2\)-coated MWNT photodetector in the dark and under AM 1.5 G illumination. The inset is the SEM image of the devices. The images are replotted from ref. 21–23. (Copyright of American Chemical Society.)

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metrics or decoration with metal particles provide viable routes to the same end. For example, Hsu et al. reported an integration of multi-walled carbon nanotubes (MWCNT) and TiO2 shells to form radial Schottky barriers in a core–shell fashion (Fig. 2c). Through this core–shell design, radial Schottky barriers between carbon nanotube cores and TiO2 shells can effectively regulate electron transport, leading to ultrahigh photogain (1.4 × 104) and ultrashort response/recovery times (4.3/10.2 ms, respectively) (Fig. 2b). In addition, radial Schottky junctions and defect band absorption broaden the detection range (UV-visible) (Fig. 2d).

In the view of optics, the performance of nano-photonic electronics can be enhanced by employing the nanophotonic technique, which supports a sophisticated management of light. For example, the technique of photon management using nanostructures has been widely used to boost the efficiency of photodetectors, light-emitting diodes, and solar cells. Considering the surface effect of metal oxide materials, light absorption near the surface is much more efficient than absorption in the deeper region of the bulk. As such, a resonant mode capable of near-surface light concentration is preferred, which can prevent intrinsic optical losses. Recently, we demonstrate a resonant scheme that can facilitate light-matter coupling by exciting resonance within multishelled hollow ZnO nanoshells. Due to the resonance-assisted effect from the concentric shells, the nanoshells can absorb >90% of UV light as compared with an equivalent volume of bulk counterparts. The nanoshell devices show enhanced optoelectronic performance and omnidirectional detectability both for incident angle and light polarizations. The general design principles behind the multishelled hollow ZnO nanoshells pave a new way to improve the performance of sophisticated nanophotonic photodetectors.

By introducing high-crystallinity metal oxide materials, one can eliminate the surface effect so as to improve the stabilities of photodetectors for uses in extreme conditions. For example, Wei et al. demonstrate a fully-transparent photodetector based on β-Ga2O3, which is capable of being operated under high temperature (700 K) and high voltage (200 V) conditions without breaking down. They show that under different oxygen concentrations (i.e. vacuum (10−5 Torr), air, and pure oxygen), the performance of metal oxide photodetectors does not change significantly, indicating that the photocurrent is not dominated by the surface effect due to the superior crystal quality. This study demonstrates an effective way to fabricate photodetectors for uses in extreme operational conditions.

Another field related to surface effect is harsh electronics, which is an emerging field aiming to promote device capability in strict environment conditions. Specific industrial applications, including oil, gas, geothermal, aircraft/automotive engines, and aerospace/military require this type of device for operating in extremes of radiation, pressure, temperature, shock, and chemically corrosive liquid/gaseous environments. To develop optoelectronics for harsh environments, we recently showed that the photodetectors made by AlN can work at temperatures up to 300 °C with radiation tolerance up to 1015 cm2 of 2 meV proton flux because of its superior thermal stability and high radiation resistance. To further improve the performance in harsh environments, introduction of multiple quantum wells (MQWs) into solar cells can enhance the efficiency by 0.52%/°C and exhibit superior radiation robustness (lifetime 430 years under solar storm proton irradiation) due to their strong atomic bonding and direct-bandgap characteristics. This study also provides valuable routes for future developments in self-powered harsh electronics.

### 2.2 Surface effect in metal-oxide memory devices and their passivation

Resistive random access memory (ReRAM), one of the potential candidates for next-generation memory, has attracted intensive attention owing to its non-volatility, high read/write speed, high density, and low power consumption. ReRAM is promising for the simplicity of device structure, ease of device fabrication and comparability to be fabricated on different types of substrate. An interesting example is the new type ReRAM recently demonstrated on the “paper” substrate, which is constructed by a simple metal-insulator-conductor structure (Ag/TiO2/C) using all-printing techniques (Fig. 3a). This study shows that the ReRAM is readily fabricated on any flexible substrates and labelled on electronics or living objects for multifunctional, wearable, on-skin, and bio-compatible applications (Fig. 3b). Recently, a cellulose-based ReRAM has demonstrated ultra-high flexibility capable of being bent down to the radius of 350 μm, which is the smallest value when
compared to any existing flexible ReRAM.35 Due to the simplicity of structure, an ultra-high memory density based on vertical-resistive random access memory is achievable.36 Retamal et al. have demonstrated that ultrathin sidewalls of C54-TiSi2 nanoscale electrodes can confine and stabilize the random nature of the resistive switching process by acting as the seeds for conducting nanofilament growth. As a result, with C54-TiSi2 as horizontal electrodes, a 3D-stacking memory can be achieved (Fig. 3c and d). Another advantage of the ReRAM is the low power consumption. Very recently, Kang et al. have shown that the nonvolatile memory made by BMO exhibits excellent resistive switching performance and can be operated with ultralow power consumption (i.e. 3.8 and 20 fJ) for set and reset processes, respectively.37 The lower power consumption results from the low conducting nanofilament formation energy, wherein the nanofilaments are only 10 nm in diameter and are separated by 20–30 nm spaces determined by transmission electron microscopy (TEM). Formation of nanofilaments in ReRAM devices has recently been observed by in situ TEM techniques and conductive atomic force microscopy, revealing the microscopic origin behind resistive switching and offering guidance for the design of novel ionic devices.38,39

Using metal oxide materials as active layers in ReRAMs is ideal due to their highly tuneable electric resistance and solid electrolyte characteristics.40–47 Metal oxide material systems, including perovskite-type oxides, ferroelectric oxides, binary transition metal oxides and complex metal oxide, have been demonstrated to be applicable in resistive switching.48–50 However, the surface effect, an intrinsic nature of metal oxide materials, is detrimental to device applications because of the induced electrical instability.51–54 Because the resistive switching mechanism is associated with the formation/rupture of the conductive nanofilaments near the oxide-electrode interface, the switching characteristic could be influenced by the chemisorbed O2 molecules at the surfaces. The evidence is that the interaction between chemisorbed oxygen and oxygen vacancies in oxides dominates the switching features of ZnO-based ReRAM.52 The absorbed oxygen causes an increase of resistance in the high resistance state (HRS). Moreover, the surface effect becomes increasingly more pronounced during operation due to Joule heating as voltage is continuously applied. This leads to the fact that the resistive switching performances of oxide memory devices, including switching yield and resistance value fluctuation, are sensitive to ambient conditions.

Sealing and packaging are often applied to memory devices to temporarily deal with varied environmental conditions. However, to achieve long-term reliability, it is necessary to make the material as inert as possible, and thus finding approaches to achieve stable switching is of particular importance. One way to reduce the surface susceptibility is through atomic doping. For example, doping nitrogen into ZnO by employing an atomic layer deposition (ALD) technique has been proposed to improve the stability and reliability of ZnO resistive memory.55 The mechanism is that the doped nitrogen can compensate the native defects and reduce oxygen molecule chemisorption, which suppresses the surface effects on the memory switching behaviour. Consequently, the memory devices exhibit better immunity against variation in ambient conditions.

It has been shown that even during mild ambient condition changes, the performance of metal oxide memory can be greatly affected. In certain harsh conditions, the degradation of the memory performance becomes worse because some metal oxides are extremely sensitive to corrosive atmospheric exposure and surface contamination associated with corrosion attack. As an example, ZnO is chemically unstable in acetic conditions.54–57 The formic acid molecules can weaken the Zn–O bonds, leading to Zn atom dissolution processes, which spreads throughout the material until device failure occurs. Therefore, even though ZnO-based electronic and optoelectronic devices exhibit fascinating performances, severe chemical instability would hinder their practical uses. The surface/interface modification by CF4 plasma treatment improves the resistive switching characteristics of the ZnO thin films.54 This treatment not only prolongs the device endurance, but also stabilizes the switching parameters, including set voltage (Vset), reset voltage (Vreset) and reset current. Moreover, the surface modification with fluorine allows the ZnO ReRAM to withstand severe corrosive conditions (Fig. 4a and b). Improved ReRAM characteristics, high inertness to surface effect, and high durability in acidic environments are due to surface passivation (saturating the dangling bonds and diminishing the oxygen vacancies) and strong Zn–F bonding (preventing the Zn atoms from dissolution) via fluorine incorporation. The ability of the devices to operate in various ambient conditions, including chemically harsh conditions, with long-term durability and reliability will play an important role in the successful emergence of resistive memory based on ZnO.

A new approach to protect the memory from environmental interference is to apply two-dimensional (2D) passivation using atomically thin 2D nanomaterials. 2D materials are the thinnest functional nanomaterials regarded as attractive substitutes to many traditional materials.59–66 Recently, Yang et al. reported that by introducing graphene electrodes as a passivation layer the surface effect in memory can be suppressed via eliminating the detrimental effect from the chemisorbed O2 molecules.51 As tested in different atmosphere, ZnO with

![Fig. 4 Box and whisker plots for the atmosphere-dependent resistance in HRS and LRS of (a) pristine ZnO. (b) F-modified ZnO devices. Copyright 2014, Nature Publishing Group.](image_url)
graphene as a passivation layer shows a lower variation in switching yield (yield ranging from 66.7% to 75.0%) compared to that of pristine ZnO (yield ranging from 41.7% to 66.7%) (Fig. 5a and b). In addition, due to the low sheet resistance and high optical transparency of graphene, ZnO memory devices exhibit not only stable resistive switching characteristics but also excellent transparency (less than 2% absorbance by graphene) (Fig. 5c).

Although the surface effects are mostly unfavourable to memory devices, well-controlled effects can help to promote the performance of memory. Recently, Durán Retamal et al. showed that the photoelectrical and resistive switching properties of ZnO ReRAM can be tuneable by treatment of ultraviolet (UV) illumination. Based on the regulation of oxygen photodesorption and readsorption by UV illumination, the treatment can significantly reduce the variations of resistance in high resistance state, the set voltage and reset voltage by 58%, 33%, and 25%, respectively.  

This finding gives physical insight into designing a stable resistive memory device in the future.

2.3. Applying the surface effect in gas sensors

From the photodetectors to memory devices, it has been shown that the electronic and optoelectronic properties of metal oxide-based devices can be significantly influenced by engineering the electronic states at surfaces. The mechanism is due to the gas adsorption, which tunes the electronic band bending at the surface, and apparently, gases in different classes can produce various effects. Based on this mechanism, gas sensors are achievable through a proper design of the metal oxide devices. There is a strong interest in the development of lightweight gas sensors capable of sensing chemicals in the parts per million (ppm) range with low-power consumption. It has been demonstrated that metal oxide-based sensors are capable of detecting gases, such as NO2, NH3, NH4+, CO, CO2, H2, H2O, O2, H2S, and C2H5OH, with high sensitivity. The fundamental mechanism of the gas sensor is the change in conductivity via electron trapping and releasing on the surface. In principle, as gas molecules are adsorbed on surfaces, charge transfer occurs that modifies the carrier concentration, resulting in a change of conductivity. For example, with NO2 or O2 adsorption, the molecules tend to capture free electrons on the surface, forming a low-conductivity depletion layer near the surfaces, which decreases the conductivity of ZnO devices. On the other hand, reductive gases, such as ethanol, H2, CO, and H2S, react with the charged oxygen molecules on surfaces, and thus free electron concentration is increased due to oxygen desorption, leading to an increase of conductivity.

Because the gas sensing mechanism relies on the surface effects, the sensitivity of the sensors can be improved by surface modifications, which could enhance the surface effect. For example, the sensitivity of ZnO to H2 sensing can be improved by Pd cluster decoration on the device surface. The addition of Pd catalytically helps the dissociation of H2 into atomic hydrogen, increasing the sensitivity of the sensor device. The sensor can detect hydrogen in concentrations down to 10 ppm, whereas there is no response to O2. The same concept also works on ZnO NWs gas sensors, whose H2 detection sensitivity can be promoted by Pt coating. Electrode selection is another way to improve the gas sensor. For example, by using Pt interdigitating electrodes, a metal oxide sensor with good ethanol sensitivity and fast response at 300 °C has been demonstrated. Introducing heterojunctions to create hybrid nanomaterials is another strategy to improve the sensitivity. He et al. have reported that the plasma-polymerized acrylonitrile/ZnO sensor offers significant advantages over conventional ZnO gas sensors. The minimum sensitivity can achieve 16.6 ppm, which is adequate for gas sensors, especially combined with a low working temperature (Fig. 6a). The results show that under UV light illumination oxygen sensing of PP-AN/ZnO NBs can be enhanced significantly because the effects of oxygen desorption/adsorption of the polymer on the electron depletion region of the ZnO is pronounced under UV light (Fig. 6b and c). The sensing behaviours of the bilayered nanomaterial demonstrated performance in terms of sensitivity and working temperature due to the adsorptive nature of the polymer.

2.4. Surface effect in metal oxide transistors

Another fundamental research area of metal oxides is thin film transistors (TFT) and NW field effect transistors (FET). The electrical tunability of metal oxide from insulator to metal, owing to the large difference in electronegativity between the heavy metal cations and oxygen atoms, has led to the development of high performance transistors with high field-effect mobility (µ), low off current (Ioff), steep subthres-
hold swings (SS) slope and large on–off current ratio ($I_{on}/I_{off}$). Many studies have shown that oxide TFTs are the best candidates as gate driver and pixel switching devices in the active-matrix of liquid crystals and organic light emitting diodes for next-generation displays. However, a common problem faced in oxide TFTs is the adverse environmental effect that results from the interaction with ambient molecules and illumination photons on the metal oxide surface. The adsorption/desorption dynamics of molecules and photons onto the exposed channel surface significantly affects performance by reducing $\mu$, increasing $I_{on}$, lowering SS, reducing $I_{on}/I_{off}$ and shifting threshold voltage ($V_{th}$) and thus becomes a critical problem for stability (Fig. 7a).

The effect of the environmental humidity on metal oxide is of special importance because oxygen and water molecules in the ambient atmosphere are known to induce the degradation of bias-stressed transistors and play an important role in carrier transport. It has been confirmed that adsorbed oxygen on the ZnO surface can capture an electron from the conduction band and that the resulting oxygen species can exist in various forms, such as $O_2^-$, $O^-$, or $O^{2-}$, as described by the following chemical reaction $O_{2(gas)} + e^- \rightarrow O_{2(ads)}$. As a result of charge transfer, a depletion layer is formed beneath the ZnO nanobelt surface, leading to reduced carrier concentration that might result in enhancement mode transistors. The surface effect manifests itself as a continuous increase in $V_{th}$ when the gate bias is kept constant over time (Fig. 7b). Assuming an exponential distribution of trap states at room temperature, $T_N$, the $V_{th}$ shift ($\Delta V_{th}$) at infinite stress time is equal to the applied gate bias required to compensate the electric field created by trapped charges before an accumulation layer is formed, yielding a stretched exponential decay for $V_{th}$ with time $\Delta V_{th} = V_0(1 - \exp(-t/\tau))$, where $\tau$ is a characteristic time constant thermally activated, $\beta$ is the dispersion parameter equal to $T/T_0$ and $V_0 = V_G - V_{th0}$, where $V_{th0}$ is the $V_{th}$ at the start of the experiment. The $\Delta V_{th}$ is also remarkably more pronounced with the variation of oxygen partial pressure and can be modelled by the Freundlich adsorption model, which states that $V_{th0}$ at oxygen pressure $P$ can be expressed as $ln(V_{th0}^P) = constant + (1/n)ln(P)$, where $n$ is constant.

Because of the wide band gap of certain metal oxides, transparent transistors can be integrated into displays. However, the surface illumination interaction effect can lead to operation sensitive to visible light irradiation. Fig. 7c shows the variation of transfer characteristic under different wavelength illumination. In contrast, regarding the surface interaction with UV illumination as explained in the PDs section, there is an advantage in using photo-transistors rather than two-terminal photodetectors due to the photo-response properties that can be modulated by gate bias. The photo-transistor is in the on-state bias the photocurrent is dominated by the photovoltaic effect and the photo-generation is minimum, because at this gate bias the dark current also increases, whereas in the off-state, the photoconductivity effect is significant for the transistor, and the photo-generation is maximum, because at this gate bias the carrier injection and thermal generation have the smallest contribution to photo-generation and in turn photo-generated current has the highest contribution just below the SS slope (Fig. 7d). However, UV illumination...
tion causes significant negative $\Delta V_{th}$, and the recovery upon turning off UV illumination is slow, leading to problems during normal device operation. The $V_{th}$ instability caused by UV illumination is attributed to positive charge trapping, whereas the slow recovery involves the recombination of oxygen vacancies, free electrons, and oxygen atoms. The energy of UV photons would help the oxygen atoms diffuse into an interstitial site. After switching off the UV illumination, the interstitial oxygen atoms require relatively high energies to diffuse back to the lattice site. This is because the diffusing oxygen atoms must overcome the potential barrier due to the surrounding ions. Therefore, it takes some time for the system to return to the initial pre-illumination state at room temperature.

Furthermore, nanoparticle decoration provides an alternative route to manipulate intrinsic properties of metal oxides via SBB modulation. Positive $\Delta V_{th}$ has been observed when decorating the metal oxide surface with either metallic or semiconducting NPs. For example, Au NPs and p-NiO NPs forming Schottky and pn nano-junctions on n-ZnO, respectively, enhance the depletion region by favouring oxygen adsorption and thus resulting in positive $\Delta V_{th}$, as shown in Fig. 8a and b. In contrast, to counteract the positive $\Delta V_{th}$ due to oxygen adsorption, thermal treatment at 100 °C can serve to prompt oxygen desorption and thus induce negative $\Delta V_{th}$ to recover the depletion region, as shown in Fig. 8b. These results highlight the versatility in tuning the depletion region of metal oxides via surface treatment and therefore its FET properties for boosting the optical and chemical sensing capabilities.

3. Conclusions

3.1. Examining the surface effects in electronics

Surface effects are pronounced in nanoscale devices and are proven to have a huge impact on the device performance. The effects could cause either a detrimental or beneficial impact based on the application of the devices. Any nanodevice subjected to the surface effect must be able to be fabricated and function stably before being commercialized. To control the effect, intrinsic capabilities and limiting factors, such as the cause of surface effect and environment interaction, should be well understood to engineer the effect. In this review, we have shown that the surface effect can be investigated electrically and optically by different types of measurements such as field-effect device measurement and UPS. However, challenges to comprehensively control the properties and maintain reliability still remain. After understanding the underlying mechanisms, one can guarantee the required level of device stability and reliability under various external conditions.

3.2. Application of surface effect in devices

For metal oxide optoelectronics, the surface effect contributes to high sensitivity but reduces the response speed. Finding a solution to compensate the trade-off between sensitivity and speed is crucial for pushing metal oxide optoelectronics into real applications. In this review, we have shown different strategies, including surface modification and geometry design, to improve the response speed and at the same time keep the high sensitivity. In addition, because the depleted region is only a few tens of nanometers at the surface, most light is penetrated, absorbed in the bulk, and wasted by fast recombination. To increase effective absorption, we proposed a resonant model capable of near-surface concentration, which is preferred for metal oxide photodetectors. For memory devices, the surface effect is usually detrimental to device applications because of the induced instability. We have examined several environmental factors that could affect the performance of ReRAM, including gas absorption and corrosive sources. We show that using atomic doping, surface modification and 2D material passivation, it is possible to stabilize the performance of ReRAM from the surface effect. Because gas adsorption is the main cause of the surface effect, gas sensing is workable and promising for metal oxide devices. We have shown that by combining nanomaterials in different classes, desired device performance can be achieved and the sensitivity can be improved. The same concepts are applicable in metal oxide transistors. We have shown that by proper treatment of UV light, the surface effect can be controlled and the performance of metal oxide can be promoted.
References


Minireview