Change in crystalline structure of W18O49 nanowires induced by X-ray irradiation and its effects on field emission

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W18O49 nanowires were synthesized by thermal evaporation, and the effects of X-ray irradiation on their crystalline structure, chemical composition, and field emission properties were systematically investigated. High-energy X-ray irradiation created nanoprotrusions on the surface of W18O49 nanowires and introduced crystalline slipping in the lattice. X-ray photoelectron spectroscopy results showed that the content of lattice oxygen increased and nitrogen was incorporated into the W18O49 nanowires after X-ray irradiation. Nevertheless, a stable and high current emission still could be obtained from the W18O49 nanowires after X-ray irradiation, with a slight increase in the threshold field from 6.4 to 7.9 MV m⁻¹. The mechanism of the change in crystalline structure, chemical composition, and field emission performance of W18O49 nanowires induced by X-ray irradiation is discussed.

1. Introduction

Field emission cold cathodes have the advantages of spontaneous start-up, low-power consumption and long lifetime. They have wide application in field emission displays, microwave and radio-frequency tubes, scientific instruments and space electric propulsion, etc. Because their high aspect ratio is beneficial to field electron emission, carbon nanotubes have been widely studied for cold cathode application since their discovery. Excellent field emission properties have been reported and the field emission displays using carbon nanotubes have been demonstrated. At the same time, much attention has also been paid to other one-dimensional nanomaterials, such as ZnO nanowires, SnO2 nanowhiskers, CuO nanowires, GaN nanowires, W18O49 nanowires, etc.

Tungsten oxide is an n-type semiconductor material with promising physical and chemical properties and has been widely studied because of its potential application as gas sensors, photo-catalysts, information displays, photovoltaic conversion, and others. Tungsten oxide with nanoscale dimensions will display enhanced properties and can further widen its practical application range. Therefore, quasi-one-dimensional tungsten oxide nanomaterials have been prepared recently by various methods. Because of the high aspect ratio of its nanostructure and good electrical properties, the field emission properties of tungsten oxide nanomaterials have attracted much attention. Excellent field emission performance, including low turn-on field, high current density, good stability, and high uniformity, has been reported for various one-dimensional tungsten oxide nanomaterials.

For example, in 2003, Li et al. reported that W18O49 nanotubes and nanowires can be prepared by heating tungsten foil under vacuum conditions and investigated their field emission properties; the turn-on field was only 2.6 MV m⁻¹. Zhou et al. used two thermal evaporation processes to grow W18O49 nanotips; stable field emission with fluctuation of 2.0% at an emission current of 1200 μA over 13 hours and a low turn-on field of 2.0 MV m⁻¹ were obtained. Single-crystalline WO3 nanowires on carbon paper substrates are excellent field emitters: an ultralow turn-on field of 1.8 MV m⁻¹ and threshold field of 3.3 MV m⁻¹ have been shown, and the field emission current density reached up to 40 mA cm⁻². On the other hand, improvements in the field mission performance of tungsten oxide nanomaterials have also been studied, such as tuning the ratio of WO2 and WO2.9, electric treatment, and plasma treatment. The effect of environment temperature and atomic oxygen exposure on the field emission properties of tungsten oxide nanowires have also been reported in attempts to determine the emission mechanism of metal oxide field emitters.

These results show that tungsten oxide nanomaterial is a promising material for application as a field emitter. In some applications, field emitters can be exposed to harsh environments. For example, there is a possible high flux of high energy...
X-ray irradiation in space. Determining how the high-energy X-ray irradiation affects the crystalline structure and field electron emission properties of tungsten oxide nanomaterials is an important issue for practical application. However, there has been little research on this important issue, which still remains an open question. In this paper, W$_{18}$O$_{49}$ nanowires were prepared by thermal evaporation and then irradiated by high-energy X-rays. We focused on the effects of X-ray irradiation on the crystalline structure, chemical composition, and field emission properties of W$_{18}$O$_{49}$ nanowires to evaluate its radiation resistance as a field emitter. The corresponding mechanism is also discussed.

2. Experimental

Large-scale, high-density, and vertically aligned W$_{18}$O$_{49}$ nanowires were grown on n-type silicon substrates (electrical resistivity: 0.1 Ω cm) by thermal evaporation of tungsten powder (China Nonferrous Metal Co., purity: 99.5%). The X-ray irradiation was carried out using synchrotron radiation at the Beijing Synchrotron Radiation Facility (BSRF). The beam is composed of X-rays with energy in the range of 3–16 keV, and the flux is $\sim 10^{12}$ phs (cm$^2$ s)$^{-1}$. The three irradiation times used in this study were 5 min, 15 min, and 60 min, and the corresponding irradiation doses were $3 \times 10^{14}$, $9 \times 10^{14}$, and $3.6 \times 10^{15}$ phs cm$^{-2}$, respectively. During irradiation, the samples were positioned in a vacuum chamber with a base pressure of $\sim 1 \times 10^{-6}$ Pa using an anode probe technique. The diameter of the probe was 5 mm. The distance between the anode and the cathode was 300 μm.

3. Results and discussion

A. Characterization of W$_{18}$O$_{49}$ nanowires before and after X-ray irradiation

Fig. 1(a–c) shows typical SEM images of W$_{18}$O$_{49}$ nanowires with top-view and cross-section views. The W$_{18}$O$_{49}$ nanomaterial was in the form of nanowires. High-density W$_{18}$O$_{49}$ nanowires were vertically aligned on n-type silicon substrates. The diameter and height of W$_{18}$O$_{49}$ nanowires were approximately 20–50 nm and 4–6 μm, respectively. Fig. 1(d) shows EDS spectrum of W$_{18}$O$_{49}$ nanowires. Four elements (O, W, C, and Si) were found in the as-prepared samples, and the atomic ratio is shown in the inset. The Si signal is from the silicon substrate, and the C signal is due to surface-adsorbed carbon. The EDS results showed that the composition of the nanowires was tungsten oxide. Fig. 1(e) shows the XRD pattern of the tungsten oxide nanowires. Two obvious peaks at 23.54° and 48.10° were observed, which can be indexed to lattice planes (010) and (020) of the monoclinic W$_{18}$O$_{49}$ phase (JCPDS card no. 36-101), respectively. Thus, it can be concluded that the prepared nanowires were made of pure W$_{18}$O$_{49}$ with a monoclinic structure and their alignment was very good, which is consistent with the SEM results.
Fig. 2 shows the XRD pattern of as-grown and irradiated W$_{18}$O$_{49}$ nanowires. The XRD pattern of irradiated W$_{18}$O$_{49}$ nanowires was almost the same as that of the as-grown W$_{18}$O$_{49}$ nanowires, which indicated that chemical structure of W$_{18}$O$_{49}$ nanowires remained unchanged after X-ray irradiation. The morphology of W$_{18}$O$_{49}$ nanowires before and after X-ray irradiation was also characterized, and the results are shown in the inset of Fig. 2. No change was found in the morphology of W$_{18}$O$_{49}$ nanowires after X-ray irradiation.

Fig. 3 shows typical TEM images of as-grown and irradiated W$_{18}$O$_{49}$ nanowires. Two obvious changes in crystalline structure were found after X-ray irradiation. First, the surface of the as-grown W$_{18}$O$_{49}$ nanowires was relatively smooth, and no obvious amorphous layer was found (Fig. 3(a)). For irradiated W$_{18}$O$_{49}$ nanowires, the surface of the nanowire was covered by an amorphous layer. The surface became much rougher and nanoscale protuberances could be observed, as shown by the black arrow in Fig. 3(c). The roughening and non-crystallization of the W$_{18}$O$_{49}$ nanowire surface after X-ray irradiation was attributed to surface atom migration or evaporation at elevated temperatures caused by high-dose X-ray irradiation.

Second, the lattice atoms of the as-grown W$_{18}$O$_{49}$ nanowires were in alignment (Fig. 3(b)). The distance between adjacent crystalline planes along the growth direction was 0.378 nm, which was indexed to be the (010) plane of the monoclinic W$_{18}$O$_{49}$ phase. The inset in Fig. 3(b) is the corresponding fast Fourier transform (FFT) image. Two obvious FFT spots indexed to (010) and (010) planes were observed, which indicated that their crystallinity was good. Additionally, there were streaking lines in the FFT image, which were normal to the growth direction of the nanowires, as indicated by the white arrow in the inset of Fig. 3(b). The present streaking lines can be attributed to planar defects such as ordering of oxygen vacancy planes. After X-ray irradiation, the degree of the W$_{18}$O$_{49}$ nanowire lattice orientation decreased. The crystalline lattice slipped along the growth direction of the nanowire, as pointed out by the white arrow in Fig. 3(d). In addition, FFT spots disappeared from the FFT image for irradiated W$_{18}$O$_{49}$ nanowires (inset of Fig. 3(d)), which meant that the crystallinity of W$_{18}$O$_{49}$ nanowires decreased after X-ray irradiation.

The chemical composition of W$_{18}$O$_{49}$ nanowires before and after X-ray irradiation was characterized, and the results are shown in Fig. 4. In addition to the peaks of C, O, and W, the peak of N at 400 eV was also observed both in as-grown and irradiated W$_{18}$O$_{49}$ nanowires (Fig. 4(a)), which indicates that N existed in as-grown W$_{18}$O$_{49}$ nanowires. The content of each element is summarized in Table 1. The chemical composition of W$_{18}$O$_{49}$ nanowires changed after X-ray irradiation. First, the content of C decreased from 35.27% to 28.46% with increasing X-ray irradiation dose up to 3.6 × 10$^{15}$ phs cm$^{-2}$. It is known that C usually originates from surface-adsorbed carbon, and high-dose X-ray irradiation will cause the temperature of W$_{18}$O$_{49}$ nanowires to increase. The decrease in C content may be attributed to surface carbon desorption of W$_{18}$O$_{49}$ nanowires at elevated temperatures caused by high-dose X-ray irradiation. Second, the content of N in W$_{18}$O$_{49}$ nanowires showed a slight increase after X-ray irradiation. Similar results have been also observed for X-ray irradiation experiments on α-Fe$_2$O$_3$ nanoflakes in our previous report.
incorporation of N into nanowires was attributed to N atom diffusion at elevated temperatures caused by high-flux X-ray irradiation.

Fig. 4(b) shows the W 4f region of the XPS spectrum. From the fitting results, four peaks of W 4f and one peak of W 5p can be seen in the XPS spectrum. The two peaks observed at 35.72 and 37.87 eV correspond to the valence of W⁶⁺, and the two peaks observed at 34.20 and 36.35 eV correspond to the valence of W⁵⁺. Because the XPS spectra of W 4f for as-grown and irradiated nanowires were almost the same, we can conclude that the valence state of W in the nanowire remained unchanged after X-ray irradiation.

Fig. 4(c) shows the O 1s region of the XPS spectrum. The O 1s peak is asymmetric and can be fitted into two peaks located at 530.0 and 531.6 eV, respectively. The peak at approximately 530.5 eV is from the lattice oxygen in the W₁₈O₄₉ crystal (i.e., O–W bonds), whereas the peak at approximately 531.6 eV is from chemisorbed oxygen caused by surface hydroxyls (O–H bonds). Comparing the O 1s spectrum before and after X-ray irradiation, it can be seen that more hydroxyls were adsorbed on the surface of W₁₈O₄₉ nanowires after X-ray irradiation. Based on the fitting result of XPS W 4f and O 1s spectra, the ratio of the lattice O 1s area to the W 4f area has been calculated, and the results are shown in Fig. 4(d). The value of S_latt / S_W first increased from 0.417 to 0.444 with an irradiation dose of 9.0 × 10¹⁴ phs cm⁻² and then gradually saturated to 0.445 as the irradiation dose increased to 3.6 × 10¹⁵ phs cm⁻², which indicated that the lattice oxygen content of W₁₈O₄₉ nanowires increased after X-ray irradiation.

In summary, we observed that more oxygen was incorporated into W₁₈O₄₉ nanowires and crystalline slipping appeared along the growth direction of nanowires after high-energy X-ray irradiation. W₁₈O₄₉ is an n-type semiconductor because of oxygen vacancies, and the crystalline structure diagram of W₁₈O₄₉ nanowires before X-ray irradiation is shown in Fig. 5(a). We propose two possible processes that may account for the phenomena reported in this study. First, during the X-ray irradiation process, the residual oxygen gas can absorb high-energy X-rays. Because of the high energy of X-rays, O–O bond may be broken and split into O atoms. Second, the nanostructure may absorb X-rays and the temperature of the sample may increase. Especially considering the small size of the nanowires, the heat dissipation will be limited, and the local temperature is expected to rise to a very high level. Under such circumstances, O atoms first adsorb on the surface and then diffuse into the W₁₈O₄₉ nanowire lattice as a result of the high temperature. Because a large amount of oxygen vacancies exist in the W₁₈O₄₉ nanowires, O atoms are prone to occupy the oxygen vacancies, as shown in
Fig. 5(b). In another side, a large amount of electrons in the valence band of W18O49 nanowires will escape from the surface of nanowires when irradiated by high-flux X-rays. W18O49 is a semiconductor; large amount of electrons may not be supplied in a timely fashion from substrate to make up for the loss of photoelectrons in the valence band, which means the O–W bond will be broken. Therefore, the crystalline structure of W18O49 nanowires was unstable and can easily change under high-flux X-ray irradiation. Compared with a perfect crystalline structure, a crystalline structure with lattice defects has poorer stability. Based on the TEM results, planar defects such as ordering of oxygen vacancy planes were observed from as-grown W18O49 nanowires. The change in crystallinity of W18O49 nanowires is prone to occur along the direction paralleling the ordering of oxygen vacancy planes. Therefore, crystalline slipping was observed along the nanowire growth direction after X-ray irradiation, as shown in Fig. 5(c).

B. Field emission properties of W18O49 nanowires before and after X-ray irradiation

Fig. 6(a) shows the field emission current density versus applied electric field ($J–E$) characteristics of as-grown and irradiated W18O49 nanowires. The inset shows the corresponding F–N plots. They show straight line except for the high current region, which indicates that the field emission behavior of the prepared W18O49 nanowires follows the F–N mechanism. The nonlinearity at high current could be attributed to the space charge effect. The turn-on field ($E_{\text{turn-on}}$) is defined as the value of the applied field required to induce a current density of 10 $\mu$A cm$^{-2}$, and the threshold field ($E_{\text{threshold}}$) refers to the value of the applied field required to induce a current density of 1 mA cm$^{-2}$. The variation of $E_{\text{threshold}}$ with X-ray irradiation dose is plotted in Fig. 6(b), and the detailed values are summarized in Table 2. The $E_{\text{threshold}}$ for W18O49 nanowires first increased from 6.4 to 7.7 and 8.5 MV m$^{-1}$ after X-ray irradiation with doses of $3.0 \times 10^{14}$ and $9.0 \times 10^{14}$ phs cm$^{-2}$, respectively. Then, the $E_{\text{threshold}}$ decreased to 7.9 MV m$^{-1}$ when the irradiation dose increased to $3.6 \times 10^{15}$ phs cm$^{-2}$, a value that was still higher than that of as-grown W18O49 nanowires. This result means that the field emission performance of W18O49 nanowires became worse after X-ray irradiation.

Table 1

| Irradiation dose (phs cm$^{-2}$) | Element (at%) | $S_{\text{lattice O}}$ | $S_{\text{WCN OW}}$ |
|---------------------------------|----------------|----------------------|-------------------|
| 0                              | C 35.27 N 3.67 O 47.97 W 13.10 | 0.417                |
| $3.0 \times 10^{14}$           | C 33.58 N 4.27 O 49.99 W 12.16 | 0.436                |
| $9.0 \times 10^{14}$           | C 29.89 N 3.47 O 50.54 W 12.82 | 0.444                |
| $3.6 \times 10^{15}$           | C 28.46 N 5.02 O 51.22 W 13.01 | 0.445                |
The maximum current density ($J_{\text{max}}$) for both as-grown and irradiated W$_{18}$O$_{49}$ nanowires was measured; this value corresponds to the maximum current density before breakdown occurs. High current density (approximately 10 mA cm$^{-2}$) can be obtained for as-grown and irradiated W$_{18}$O$_{49}$ nanowires (Table 2). No obvious degradation of the maximum current density was observed after X-ray irradiation. The field emission stabilities of as-grown and irradiated W$_{18}$O$_{49}$ nanowires were also tested, and the results are shown in Fig. 6(c). The emission current density gradually increased with time, and no degradation was found for either as-grown or irradiated W$_{18}$O$_{49}$ nanowires. The emission current density fluctuations ($\delta$) of as-grown and irradiated W$_{18}$O$_{49}$ nanowires were calculated, and the results are summarized in Table 2. The emission current fluctuations ($\delta$) were in the range of 4–7% and no obvious relationship with irradiation dose was found. The field emission measurements indicated that after X-ray irradiation, a stable and high current emission still could be obtained from the W$_{18}$O$_{49}$ nanowires, with only a slight increase in the threshold field.
Based on field emission theory, the work functions of field emitters play an important role in field electron emission. Therefore, the work functions of as-grown and irradiated W$_{18}$O$_{49}$ nanowires were measured by X-ray photoelectron spectroscopy, and the results are shown in Fig. 7(a). The work function can be calculated using the low kinetic energy cut-off. The inset of Fig. 7(a) shows the obtained work function. The work function values were almost the same (4.60 ± 0.05 eV) for as-grown and irradiated nanowires, except for W$_{18}$O$_{49}$ nanowires irradiated with a dose of 3.6 \times 10^{15} \text{ phs cm}^{-2} (4.50 ± 0.05 eV). Obviously, the threshold field increase for W$_{18}$O$_{49}$ nanowires after X-ray irradiation was not caused by a change in work function.

Fig. 7(b) shows the C 1s region of the XPS spectra of as-grown and irradiated W$_{18}$O$_{49}$ nanowires without calibration. The intensity of the C 1s peak declined after X-ray irradiation, which means that the content of surface-adsorbed carbon decreased. At the same time, a shift in the C 1s peak to higher binding energy was also observed after X-ray irradiation, and the degree of the shift in the C 1s peak was proportional to the X-ray irradiation dose (inset of Fig. 7(b)). The shift in the C 1s peak to higher binding energy is usually attributed to charging effects induced by the poor electrical conductivity of a sample. During the process of XPS measurement, photoelectrons can escape from the sample surface, and a positive space charge can appear on the surface. If the electrical conductivity of the sample is poor, the electrons cannot be supplied in a timely fashion from the substrate to neutralize the positive space charge. This gives rise to the accumulation of positive charge on the sample surface, which is called the charging effect. Positive charges build a surface potential ($V_s$) on a sample, which will hinder electrons from escaping from the sample.

When considering the charging effect, the energy equation of the photoelectric effect can be written in the following form:

$$E_k = hv - E_b - \phi_s - eV_s$$  \hspace{1cm} (1)

where $E_k$ is the kinetic energy of a photoelectron, $hv$ is the energy of a photon, $E_b$ is the binding energy, $\phi_s$ is the work function, and $eV_s$ is the energy shift of the charging effect. The presence of surface potential leads to a decrease in photoelectron kinetic energy, and the measured binding energy of the C element will shift to a higher value.

Based on the above discussion, the shift in the C 1s peak to higher binding energy can be attributed to the charging effect induced by poor electrical conductivity of the sample. In our experiment, the C 1s peak shifted to higher binding energy after X-ray irradiation, which indicates that the electrical conductivity of W$_{18}$O$_{49}$ nanowires decreased after X-ray irradiation. The decrease in the electrical conductivity of the W$_{18}$O$_{49}$ nanowires may contribute to the increase in lattice oxygen content and crystalline slipping. First, W$_{18}$O$_{49}$ is an n-type semiconductor because of oxygen vacancies, so an increase in lattice oxygen content means the amount of oxygen vacancies decreases and the electron concentration of the conduction band decreases. Second, crystalline slipping causes the degree of disorder of the lattice structure to rise and the scattering probability for electrons in the transport process to increase, which leads to a decrease in electron mobility. This decrease in electron mobility and electron concentration will cause the electrical conductivity of W$_{18}$O$_{49}$ nanowires to become poor.

The field emission performance of a semiconductor material has a close relationship with its electrical conductivity. ZnO nanostructures with higher conductivity have better field emission performance, including lower turn-on and threshold fields. This is because they have a better supply of electrons to the emitting surface. Therefore, we suggest that the increase in threshold field was attributed to the decrease in the electrical conductivity of W$_{18}$O$_{49}$ nanowires.
conductivity of W_{18}O_{49} nanowires after X-ray irradiation, which was induced by crystalline defects and decrease in the amount of oxygen vacancy. Early studies have shown that defects or vacancies would have effects on the field emission properties of low-dimensional nanomaterials.\textsuperscript{38,39} Oxygen vacancy is the main defect affecting the electronics properties of metal oxide nanomaterials. Oxygen vacancy will form a donor state claimed by protuberances that appear on the surface of W_{18}O_{49} nanowires emission.\textsuperscript{40} A decrease in the diameter of the field emitter and thereby increase the field enhancement, which will enhance electron field emission.\textsuperscript{29,41} Therefore, the decrease in the threshold field of the W_{18}O_{49} nanowires was observed when the irradiation dose increased to 3.6 \times 10^{15} \text{ phs cm}^{-2}.

4. Conclusions

High-energy X-ray irradiation will change the crystalline structure, chemical composition, and field emission performance of W_{18}O_{49} nanowires. After X-ray irradiation, nanoscale protrusions on the surface and crystalline slipping were observed for W_{18}O_{49} nanowires. The content of lattice oxygen increased and more nitrogen was incorporated into W_{18}O_{49} nanowires after X-ray irradiation. Nevertheless, a stable and high current emission can be obtained from W_{18}O_{49} nanowires after X-ray irradiation, with a slight increase in the threshold field. This increase in the threshold field was attributed to the decrease in the electrical conductivity of W_{18}O_{49} nanowires induced by increasing lattice oxygen content and crystalline defects.

Conflicts of interest

There are no conflicts to declare.

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