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XPS studies on surface reduction of tungsten oxide nanowire film by Ar⁺ bombardment

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ABSTRACT

WO₃ nanowire film was bombarded by Ar ion beam in the analysis chamber of an X-ray photoelectron spectroscopy (XPS) system to produce uniform tungsten cone arrays. The WO₃ nanowire film itself served as an etching mask during the Ar⁺ bombardment. The changes of surface chemical states and electronic structures during bombardment were monitored by in situ XPS. The morphological evolution with different Ar⁺ bombardment time was observed by ex situ scanning electron microscopy (SEM). At the start of Ar⁺ bombardment partial W⁶⁺ in WO₃ was reduced to W⁵⁺ immediately, subsequently to W⁴⁺ and then to W^{*+} (intermediate chemical state between W⁴⁺ and W⁰), finally to W⁰. Multiple oxidation states of tungsten coexisted until finally only W⁰ left. SEM images showed that the nanowires were broken and then fused together to be divided into clusters with a certain orientation after long-time high-energy ion beam bombardment. The mechanism of the ion-induced reduction during bombardment and the reason of the orientated cone arrays formation were discussed respectively.

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1. Introduction

Tungsten trioxide (WO₃) is an important semiconductor due to its wide applications in electrochromic devices [1], gasochromic devices [2], gas sensors [3], field emission devices [4] and photocatalysts [5]. Its excellent photochromic, electrochromic and gasochromic properties are attributed to easy transformation between stoichiometric WO₃ and nonstoichiometric WO_{3-x}. Nonstoichiometric WO_{3-x} such as W₁₈O₄₉ [6] and W₂₀O₅₈ [7] consist of W⁶⁺ and W⁵⁺ as a result of inadequate oxidation in the process of sample preparation. Different tungsten oxidation states can be obtained by Ar⁺ bombardment on WO₃ nanowires owing to ioninduced reduction effect.

In XPS study Ar⁺ bombardment is used to peel away surface atoms so as to achieve the depth profile of sample composition. The exchanged energy from the high energy ion to the surface atoms results in the removal of surface atoms from the sample [8,9]. In addition to the removal of the surface layer, ion bombardment may also cause other effects such as preferential sputtering, implantation of bombardment particles, gross surface heating and ion-induced reactions [8]. The preferential sputtering is caused by different sputtering rates of individual constituents.

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The implantation of bombardment particles into the surface is realized at lower sputtering rate of the bombarded components. The gross surface heating is caused by the interaction between the surface material and the high energy incident ions. In the ioninduced reduction process, the ion energy transferred to the lattice atoms may exceed the binding energies in molecules by several orders of magnitude, which therefore suffices to break up chemical bonds and to create new ones [9,10]. These side effects of ion bombardment can make depth profile analysis more complicated. The preferential sputtering usually causes errors in the components' depth profile analysis. In particular, the chemical states of some metal oxides are difficult to be estimated in a depth profile because of the ion-induced reduction. For many transition metal oxides such as TiO₂ [11], V₂O₅ [12], Ni₂O₃ [13], MoO₃ [14], WO₃ [15], CeO₂ [16] and PdO [8] the reduction to the corresponding metal or lower valence oxide is often observed under ion bombardment.

In previous work [17], we obtained completely metallic W cone arrays from WO₃ nanowire film by long-time Ar⁺ bombardment with WO₃ nanowire film itself serving as the etching mask. The field-emission measurements indicated that the tungsten cone arrays had a better performance of field emission than that of WO₃ nanowire film. In the process of Ar⁺ bombarding on WO₃ nanowire film the change of W chemical states and the morphological change from nanowires to cone arrays should be concerned.

In this work the whole ion-induced reduction process of WO_3 nanowires was monitored by in situ XPS measurement to study the evolution of tungsten chemical states. W^{5+} oxidation state

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appeared immediately when the bombardment began, an intermediate chemical state between W⁴⁺ and W⁰, W^{x+} started to appear from 140 s of bombardment, and from 160 s on, all oxide states of W including W⁶⁺, W⁵⁺, W⁴⁺, W^{x+}, W⁰ coexisted until there was only W⁰ in the end. The morphological change of the samples with different Ar⁺ bombardment time was observed by ex situ SEM. SEM images revealed that the nanowires were broken and then fused together to be divided into wire cluster with a certain direction after long-time high-energy ion beam bombardment due to the long-time gross heating effect.

2. Experiment

Stoichiometric WO₃ nanowire film was prepared on silicon substrate by thermal evaporation method (details in Ref. [18]). The WO3 film was loaded into Thermo Fisher Scientific ESCALAB 250 XPS system, where Ar⁺ bombardment was performed and surface chemical state of the sample was characterized. XPS spectra were recorded using a monochromated Al Kα (1486.6 eV) X-ray source with the take-off angle of 90° after different Ar⁺ bombardment time. The energy resolution of the instrument at 20 eV of pass energy is 0.6 eV, as estimated from the full width at half maximum (FWHM) of Ag 3d_{5/2} peak. The Ar⁺ bombardment was operated with EX05 argon ion gun whose angle arrangement given the sample surface normal is 45° at a chamber pressure of 1×10^{-6} Pa. The ion beam voltage was 3 kV and the emission current was 2 µA. The etching area was $2 \text{ mm} \times 2 \text{ mm}$, which was much larger than X-ray spot (320 µm in diameter). The spectra in this paper were calibrated using W4f_{7/2} peak of WO₃ at 35.6 eV.

In order to observe the morphological change during Ar^+ bombarding on WO₃ nanowire film, the surface morphology of the samples with different Ar^+ bombardment time were observed by field emission environmental SEM (FEI Quanta 400F) whose energy of the primary electron beam was 20 kV with the Everhart-Thornley detector. The samples for SEM observation were taken out from the UHV chamber after WO₃ nanowire film was bombarded for a period of time.

The composition and chemical states changes induced by Ar⁺ bombardment were analyzed by XPS. The W4f core levels were recorded with a step of 0.05 eV and a pass energy of 20 eV. The Shirley-type background due to inelastic scattering electrons was taken into account. The XPS spectra of W4f core level were fitted into peak doublets with parameters of spin–orbit separation ΔE_P ($4f_{5/2}-4f_{7/2}$) = 2.1 ± 0.1 eV and intensity ratio $I_{W4f_{5/2}}/I_{W4f_{7/2}}$ = 0.75 using Thermo Avantage v4.30 software. The ratio of Lorentzian to Gaussian varied in the range of $30 \pm 5\%$ and the spectra of pure metallic W were asymmetric ascribed to the coupling of the core hole with the Fermi sea whose asymmetric parameters were used in fitting metallic W state. The asymmetric peak shape was determined using the equation [19]

$$T = TM \cdot CT + (1 - TM)exp(-D_x \cdot ET)$$
(1)

where D_x is the separation from the peak center in channels, ET is the exponential tail, TM was the tail mixing ratio, CT is the constant tail height. For metallic W state the values of ET, TM and CT were 0.0373, 77.7% and 0, respectively.

W5p_{3/2} peak was in the higher BE (binding energy) side of W4f_{5/2}. W5p_{3/2} invariably accompanied with W4f peak and their relative peak position and intensity were nearly unchangeable. The relationships between the BE and peak intensity of W5p_{3/2} and W4f_{7/2} were as follows: BE_{W5p_{3/2} = BE_{W4f_{7/2} + 5.8, *I*_{W5p_{3/2}/*I*_{W4f_{7/2} = 0.08 as shown in Fig. 1a and Table 1. Due to the mixing effect of the ion beam the full width at half maximum (FWHM) of W⁶⁺ peak were larger than those of WO₃ nanowires film at the initial bombardment state (before 70 s of bombardment time). For WO₃ nanowires}}}}

film before Ar⁺ bombardment FWHM of W4f_{7/2} was 1.0 eV, while FWHM of W4f_{7/2} in W⁶⁺ oxidation state was 1.8 eV at 300 s of bombardment time. These parameters are summarized in Table 1.

3. Results and discussion

3.1. XPS analysis

3.1.1. W4f core level spectra

W4f core level XPS spectra of WO₃ nanowires with different reduction degrees were obtained by Ar⁺ bombardment on the same WO₃ nanowire film (Fig. 1a–k). During Ar⁺ bombardment the peak BE (binding energy) of W4f_{7/2} and the spectral line-shape of W4f core level varied drastically. The W4f_{7/2} peak BE shifted from 35.6 eV of the initial WO₃ nanowire film to 31.0 eV of the final etched sample. Intermediate oxidation states were observed in the reduction process of WO₃ to metallic W. The spectral shape of W4f core level changed from narrow doublet peaks to broad bands which included several oxidation states of W, in the end the W4f spectra changed into narrow doublet peaks corresponding to metallic W.

In order to understand the evolution process of W oxidation states change, the spectra with different Ar⁺ bombardment time were fitted on the basis of the parameters in Table 1. Fig. 1a shows a W4f XPS spectrum of the stoichiometric WO3 nanowire film before Ar⁺ bombardment where only W⁶⁺ spin-orbit doublet existed. W⁵⁺ oxidation state emerged immediately after the bombardment (Fig. 1b). A couple of peaks assigned to W⁴⁺ oxidation state appeared with the bombardment time increasing to 70 s (Fig. 1c). After 140 s of bombardment a new W chemical state with W4f_{7/2} peak BE of 31.9 eV began to appear (Fig. 1d). The spectrum could not be well fitted without the addition of a fourth component (Fig. 1d, 140 s). From 160 s on, metallic W⁰ was presented (Fig. 1e). With a fourth component it was possible to well fit the spectra in Fig. 1d and e. The fourth component had a BE between W⁴⁺ (33.2 eV) and W^0 (31.1 eV) which was assigned as W^{x+} in this work. Similar situation was observed when Ar⁺ bombarded to V₂O₅ pellet where V^{2+}/V^{1+} presented [12,20]. Subsequently, from 160 s to 4800 s, various tungsten oxidation states including W⁶⁺, W⁵⁺, W⁴⁺, W^{x+} and W⁰ coexisted (Fig. 1f-i). From 4800 s on, only metallic W⁰ doublet peaks with W4f_{7/2} peak BE at about 31.0 eV was observed (Fig. 1j and k).

By analyzing the W4f core level XPS spectra from 140 s to 4800 s (Fig. 1d–j), the W4 $f_{7/2}$ peak of W^{x+} was related to the shape of the curve in the range between 30.0 eV and 32.5 eV. Compared with pure metallic W state in Fig. 1j, the tail height of the curve in this range was much higher in Fig. 1e-i. When fitting this range with the same asymmetric parameters of the pure metallic W, there should be a W^{x+} peak centered at 32.0 eV. Increasing the bombardment time to 4800s the tail heights of the curve in the range between 30.0 eV and 32.5 eV dropped to zero where only W⁰ existed. It was concluded that the W^{x+} state should be an intermediate state between W⁴⁺ and W⁰, which might originate from the W³⁺, W²⁺ or W¹⁺ oxidation state. W^{x+} may also originate from the tungsten ions with partial unbroken oxygen ions and W-W bonds. Or there would also be 'beta' shift induced from species adjacent to the ion attached to the photoionized W atoms to form this intermediate chemical state. It is difficult to assign the intermediate chemical state to a specific formal oxidation state.

The evolution of the concentrations of the different tungsten chemical states as function of Ar⁺ bombardment time is shown in Fig. 2, expressed in percentage of the total W4f_{7/2} signal. The most drastic changes could be found in the first 160 s. The W⁶⁺ decreased drastically, W⁵⁺, W⁴⁺, W^{x+} and W⁰ appeared gradually. The content of W⁶⁺ decreased to zero after WO₃ nanowire film was bombarded



Fig. 1. Representative fitted W4f core level spectra under $3 \text{ kV} \times 2 \mu \text{A}$ Ar ion gun bombarding on WO₃ nanowire film after different Ar⁺ bombardment times: (a) 0 s; (b) 10 s; (c) 70 s; (d) 140 s; (e) 160 s; (f) 300 s; (g) 500 s; (h) 1500 s; (i) 3000 s; (k) 8400 s.

for 4800 s, the contents of the intermediate W oxidation states (W^{5+}, W^{4+}, W^{x+}) increased and then decreased to zero, whereas W^0 increased all the time. The O/W ratio at the different oxidation stages is shown in Table 2. The O/W ratio was calculated using the Scofield sensitivity factor method where the Scofield sensitivity factors of W4f and O1s are 8.22 and 2.93, respectively. During the initial 70 s, the O/W ratio was close to the stoichiometric ratio of WO₃. However the chemical states of W changed significantly

when W^{5+} and W^{4+} appeared as shown in Figs. 1 and 2. The O/W ratio decreased gradually along with Ar^+ bombardment process, and there was still O element remained in the sample at the final stage. During the Ar^+ bombardment process the oxygen content reduced due to the preferential sputtering of oxygen in the metal oxide compound.

At present in literature the reduction of metal oxides is mostly explained by the preferential sputtering of oxygen in the metal

Table 1

Overview of the W4f main and W5p _{3/2}	peak fit parameters for d	lifferent tungsten oxidation states.
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Tungsten oxidation states	$W4f_{7/2}\;\text{BE}\left(eV\right)$	%L-G	FWHM (eV)	$\Delta \text{BE}(\text{eV})(\text{W4f}_{7/2}\text{-}\text{W4f}_{5/2})$	$I_{\rm W4f_{5/2}}/I_{\rm W4f_{7/2}}$	W5p _{3/2} BE (eV)	$I_{\rm W5p_{3/2}}/I_{\rm W4f_{7/2}}$
W^{6+} W^{5+} W^{4+} w^{x+} $^{a}W^{0}$	$\begin{array}{c} 35.6 \pm 0.1 \\ 34.3 \pm 0.2 \\ 33.2 \pm 0.2 \\ 32.0 \pm 0.2 \\ 31.0 \pm 0.1 \end{array}$	30 ± 5	^b 1.8 ^c 1.5 1.5 1.2 0.8	2.1 ± 0.1	0.75	$\begin{array}{l} 41.30 \pm 0.1 \\ 40.10 \pm 0.1 \\ 39.00 \pm 0.1 \\ 37.80 \pm 0.1 \\ 36.75 \pm 0.1 \end{array}$	0.08

^a The asymmetric peak-shape parameters of the metallic W: exponential tail (ET) is 0.0373, tail mixing ratio (TM) is 77.7%.

^b Before 70 s of bombardment FWHM of W⁶⁺ is 1.0 eV because there is no serious mixing effect induced by ion beam bombardment.

^c Before 70 s of bombardment FWHM of W⁵⁺ is 1.0 eV without serious mixing effect induced by ion beam bombardment.

The O/W ratio during the whole Ar⁺ bombardment process.

Bombardment time (s)	0	10	70	140	160	300	500	1500	3000	4800	8400
O/W ratio	73:27	73:27	73:27	71:29	68:32	65:35	64:36	57:43	53:47	24:76	16:84

oxide compounds. However, our results showed that part of WO_3 was reduced to W^{5+} and W^{4+} in the initial stage of Ar^+ bombardment while O/W ratio remained unchanged. The first stage of ion bombardment led to partial break of the W–O bonds. The oxygen split off in this way did not necessarily leave the surface; instead, it might remain at interstitial lattice sites of the surface layer. There was no contradiction that the observed reduction of the O1s intensity is slower than the change of the tungsten valence states as shown in Fig. 2 and Table 2. This also happened for MoO₃ [9]. Based on above analysis one conclusion was reached: the ion-induced reduction is not necessarily caused by the preferential sputtering of oxygen.

The first ion-induced reduction study in XPS was presented by Kim et al. [8]. They proposed a model based on bulk thermodynamic free energy considerations to explain the reduction of metal oxides to the corresponding metal or lower valence oxides. All oxides whose $-\Delta G_{\rm f}^{\circ}$ value at room temperature were below a certain value could be reduced by exposure to Ar ions whereas those oxides with $-\Delta G_{\rm f}^{\circ}$ above another definite value were stable to this exposure. Using Kim's proposed model we calculated the energy of Ar ion beam and the required energy for the transformation from WO₃ to lower valence WO₂ and metallic W, respectively. The energy of Ar ion beam ($E_{\rm Ar^+}$) sputtering for a period of time (t) was calculated by

$$E_{\rm Ar^+} = I \times U \times t \tag{2}$$



Fig. 2. Evolution of the different tungsten oxidation states as function of Ar^+ bombardment time. The inset shows the first 500 s in more detail.

where I (A) is the emission current of Ar ion beam, U (V) is the ion beam voltage, t (s) is the duration of Ar⁺ bombardment. The required energy for WO₃ to lower valence WO₂ and metallic W (E_{Trans}) is calculated by the following equation:

$$E_{\rm Trans} = \frac{\rho \times V}{M} \times \Delta_{\rm r} H^{\circ} \tag{3}$$

where ρ (g/cm³) is the density of WO₃, V (cm³) is the etched region volume by Ar⁺ bombardment, M (g/mol) is the molecular weight of WO₃, $\Delta_r H^\circ$ is the standard molar heat of reaction from WO₃ to lower valence WO_x and metallic W at 298.15 K in kJ/mol.

W⁴⁺ started to appear after 70 s of bombardment (shown in Figs. 1c and 2). The energy of Ar ion beam (E_{Ar^+}) and the required energy (E_{Trans}) from WO₃ to lower valence WO₂ were calculated using Eqs. (2) and (3), respectively. The energy of Ar ion beam (3 kV, 2 μ A) was 4.2 × 10⁻¹ J calculated by Eq. (2) where *I* was 2 × 10⁻⁶ A, *U* was 3 × 10³ V, and *t* was 70 s.

As for E_{Trans} we should obtain the standard molar heat of reaction transformed from WO₃ to lower valence WO₂ ($\Delta_r H^\circ$) which was determined by the standard molar heat of formation ($\Delta_f H^\circ$) at 298.15 K of the reactants and products in the following reaction

$$WO_3 \rightarrow WO_2 + (1/2)O_2$$

where the $\Delta_{\rm f} H^{\circ}$ values of WO₂, O₂ and WO₃ are -589.7 kJ/mol, 0 kJ/mol and -842.9 kJ/mol [21]. The value of the standard molar heat of reaction $\Delta_r H^\circ$ is 253.2 kJ/mol calculated by the above $\Delta_f H^\circ$ values. The number of moles of WO₃ etched by Ar⁺ bombardment was given by $(\rho \times V)/M$, where ρ of WO₃ is 7.16 g/cm³ and M is 231.85 g/mol of WO₃. The etched region volume V is 4×10^{-8} cm³ estimated by the product of etched area $(2 \text{ mm} \times 2 \text{ mm})$ and the etched depth is 10 nm for 70 s (the etched depth is obtained from the calibrated etching rate 0.154 nm/s for SiO₂ under the same Ar⁺ bombardment condition). Putting the above values into Eq. (3), $E_{\rm Trans}$ from WO₃ to WO₂ in the etched region for 70 s was 3.1×10^{-4} J. Compared with the energy of Ar ion beam ($E_{\rm Ar^+}$) and the required transformation energy (E_{Trans}) from WO₃ completely to WO₂ in the etched region, the value of $E_{\rm Ar^+}$ was about 1000 times as that of E_{Trans} from WO₃ to WO₂ shown in Table 3. This result indicated that the energy required from WO_3 to WO_2 was only a very small fraction of the Ar⁺ beam energy.

After 4800 s of bombardment WO₃ was transformed into metallic W completely as shown in Figs. 1j and 2, the values of E_{Ar^+} and E_{Trans} from WO₃ to metallic W (see Table 3) were 2.9×10^1 J and 7.7×10^{-2} J, respectively where $\Delta_r H^\circ$ of the reaction WO₃ \rightarrow W+(3/2)O₂ was 842.9 kJ/mol and the etched depth 740 nm for 4800 s was estimated from the calibrated etching rate of SiO₂ at

116 **Table 3**

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1	· · · · · · · · · · · · · · · · · · ·	for a MO to loop loop 1 and MI states	(Γ)) $f_{res} = 1.66$ and $f_{res} = 1$ and $f_{res} = 1.66$
ne energy of Ar ion beam (E _{Aut})) and the reduired transformation energ	v from vvu ₂ to lower valence vv states	(Errang) for different pomparament time.
	,	,	

Bombardment time	Energy of Ar ion beam/ $E_{\rm Ar^+}$	Involved reaction	Required transformation energy/E _{Trans}
70 s 4800 s	$\begin{array}{l} 4.2 \times 10^{-1} J \\ 2.9 \times 10^1 J \end{array}$	$ \begin{array}{l} WO_3 \rightarrow WO_2 + (1/2)O_2 \\ WO_3 \rightarrow W + (3/2)O_2 \end{array} $	$\begin{array}{l} 3.1\times 10^{-4}J\\ 7.7\times 10^{-2}J \end{array}$

0.154 nm/s. The value of $E_{\rm Ar^+}$ was about 350 times as that of $E_{\rm Trans}$ from WO₃ to metallic W.

From above calculation the energy of Ar ion beam exceeded by several orders of magnitude the required transformation energy from WO₃ to lower valence states, which was in agreement with Holm's proposed opinion [9,10]. Holm et al. considered the energy received by the lattice atoms from the bombarding ion might exceed by several orders of magnitude the binding energies in molecules so that chemical bonds could be broken. Theoretically the reduction of all metal oxides could happen while there was no ion induced reduction of Al₂O₃, MgO, ZnO, SnO₂, Ga₂O₃, In₂O₅ and SiO₂ in experiments. The ion-induced reductions were observed in some metal oxides, which indicated that most of the energy of Ar ion beam was used to remove the surface atoms and the ion-induced reduction was merely a side-effect of ion bombardment for some compounds. Therefore the reaction heat involved during Ar⁺ bombardment was not the main reason for ion-induced reduction.

The ion-induced reduction of some metal oxides by ion bombardment was very complicated which could not be explained simply by the preferential sputtering of oxygen and the reaction heat involved in ion bombardment independently. For the ion-induced reduction of WO_3 we believe that the more



essential reason was the varied valence states of W element which led to the coexistence of multiple oxidation states in XPS W4f core level spectra besides the preferential sputtering of oxygen was an important factor. Various oxidation states had been observed in many transition metal oxides such as MoO₃, ReO₃, TiO₂, V₂O₅ and ZrO₂ after Ar⁺ bombardment. A small amount of Ti³⁺ had been observed even in the case of 10 V bombardment for TiO₂ sample [11]. Ion-induced reduction of oxides should be associated with the inherent properties of elements in oxide compounds, such as transition metal's electron occupied states of d or f orbits, the varied valences of the composed metal constituents in oxides, the value of M–O (metal–oxygen) bond energy in oxide compounds, besides the preferential sputtering of oxygen. Detailed studies about ion induced reduction of oxides were reported in our other work [22].

3.1.2. XPS valence band spectra

The XPS valence band spectra were used to characterize the surface electronic structure of the materials. The energy bands within the valence band of WO₃ have almost entire characteristics of tungsten 5d or oxygen 2p orbital [23]. The typical XPS valence band spectra of WO₃ nanowires film at different bombardment time are shown in Fig. 3. Fig. 3a shows the XPS valence band spectrum of



Fig. 3. XPS valence band spectra of the different bombardment time on WO_3 nanowire film: (a) 0 s; (b) 70 s; (c) 160 s, (d) 300 s; (e) 3000 s; (f) 8400 s.



Fig. 4. The surface morphologies of the different bombardment time during Ar⁺ bombardment on WO₃ nanowire film: (a) 0s; (b) 300s; (c) 500s; (d) 1500s; (e) 3000s; (f) 4800s; (g) 8400s; (h) magnified image of g.

pure WO₃ nanowire film. Compared with the literature results [24], the spectrum in Fig. 3a was characteristic of a monoclinic phase γ -WO₃ consistent with the results from Raman analysis in our previous work [18]. Covalent bonding interactions transformed O2p and W5d orbitals into bonding and antibonding orbitals. The peak located at ~4.1 eV was assigned to an O2p-derived band while the peak centered at ~6.2 eV corresponded to a hybridized 'W5d–O2p' band. The onset of the valence band spectrum at ~2.5 eV could be assigned to the valence band maximum (VBM).

A new peak near the Fermi level appeared in the XPS valence band spectrum of the sample after the WO₃ nanowire film was bombarded for 70 s (Fig. 3b). As shown in Fig. 1c, there were W^{5+} and W^{4+} together with W^{6+} in this sample so that residual W5d electrons appeared. Due to the empty conduction band of tungsten oxide associated with the W5d electrons [25], the peak near the Fermi level was attributed to the conduction band filled with the residual W5d electrons which was associated with lower oxidation states.

At the bombardment time of 160 s, the edge of the Fermi level appeared at 0 eV where metallic W started to emerge (Fig. 3c) and the peak of O2p decreased a lot compared with that of pure WO₃ nanowires film. Once metallic W came into existence the peak near Fermi level corresponding to W5d electrons became not obvious because the density of metallic W increased. The intensity of the hybridized W5d–O2p decreased while the density of the metallic W increased with the increase of Ar⁺ bombardment time (Fig. 3d

and e). Fig. 3f corresponds to the metallic W which had a sharp edge of the Fermi level. The O2p and hybridized W5d–O2p disappeared in the valence band spectrum of metallic W. In conclusion, the XPS valence band spectra further confirmed the results of W4f core level XPS spectra.

3.2. SEM surface morphology characterization

The surface morphologies of the WO₃ nanowire film (Fig. 4a) and the samples obtained from Ar⁺ bombardment on the same batch of WO₃ nanowire film for different time were investigated by SEM. Using thermal evaporation method high density WO₃ nanowires were prepared on the silicon substrate. The average length of WO₃ nanowires was about $4 \,\mu m$ and the diameter varied from 50 to 80 nm. The WO₃ nanowires had a random distribution on the surface of the silicon substrate. Though the W4f core level XPS spectrum changed significantly from narrow doublet peaks to very broad spectrum shown in Figs. 1 and 2, the morphology of the sample after 300s of bombardment was similar with that of the as-prepared WO₃ nanowire film which had a random distribution without obvious change (Fig. 4b). For the sample after 300 s of bombardment W⁶⁺, W⁵⁺, W⁴⁺, W^{x+}, W⁰ coexisted as shown in Fig. 2f. For the sample after 500 s of bombardment the morphology has changed slightly with some of the wires broken or bent by continuous Ar⁺ bombardment (Fig. 4c). After 1500 s of bombardment the wires were broken and started to be divided into wire clusters with a certain orientation because the long-time high-energy ion beam bombardment provided enough energy to fuse the broken wires together (Fig. 4d). The chemical states of W were W⁰, W^{x+} and W^{4+} together with a small amount of W^{5+} and W^{6+} are shown in Figs. 1h and 2. The initial morphology of cone arrays emerged after 3000s of bombardment. The cones were consisted of many broken wires fused together with apparent gaps inside (Fig. 4e). After 3000 s of bombardment, there was mostly W⁰ with small amounts of other residual W oxidation states (Figs. 1i and 2). The cones became sharper after 4800s, and the wires were further fused together with gaps smaller than that of the sample after 3000 s (Fig. 4f). Only metallic W was observed after 4800 s. In the end, metallic tungsten cone arrays with a uniform orientation were obtained after 8400s, the wires was completely fused together without any slit on the cones (Fig. 4g and h) and the tungsten chemical state did not change any more even if ion bombardment time was increased.

The morphological change during Ar⁺ bombardment was in agreement with the schematic diagram of the ion sputtering process proposed in our previous work [17]. In brief, the top ends of the nanowires served as the etching mask when ion beam bombarded the sample. Some of ion beam bombarded the top ends of the wires to break them down, and the others entered into the gap between the wires to divide the wires into some clusters. Because the high-energy Ar⁺ beam was orientated at an incident angle of 45°, the nanowires started to be divided into clusters with a certain direction. The long-time high-energy ion beam bombardment provided enough energy to fuse the broken wire cluster together and finally orientated cone arrays was obtained. The main formation mechanism of the orientated cone arrays was the gross surface heating produced by ion bombardment. The gross surface heating of long-time ion bombardment caused the nanowires to be broken and fused together. The morphological change was much slower than the change of tungsten chemical states because the energy used to break the nanowires was provided by gross surface heating of long-time ion beam bombardment whereas W-O chemical bonds were broken immediately once ion beam hit the WO₃ nanowires film. The uniform orientation of cone arrays was caused by the fixed incident angle of 45° of the high-energy Ar ion beam. Therefore the formation of the directional cone arrays was the long-time gross surface heating of ion bombardment with the orientated high-energy Ar ion beam emitted by EX05 ion gun.

4. Conclusions

In summary, WO₃ nanowire film was reduced to metallic W by Ar⁺ bombardment through a complicated process of chemical state change of tungsten. During Ar⁺ bombardment the content of W⁶⁺ decreased to zero, the contents of the intermediate oxidation states of W (W⁵⁺, W⁴⁺, W^{x+}) increased and then decreased, the content of W⁰ increased all the time until the chemical state changed into metallic W after long-time Ar⁺ bombardment. Ion-induced reduction of WO₃ should be associated with the varied valence states of W element besides the preferential sputtering of oxygen.

The different surface morphologies after the different etching time during Ar^+ bombardment on the WO₃ nanowire film was explained by the same mechanism proposed in our previous work. The WO₃ nanowire film itself served as an etching mask to produce tungsten cone arrays due to the long-time gross surface heating of ion bombardment with the orientated high-energy Ar ion beam.

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