

Nanostructures on Sapphire Surfaces Induced by Metal Impurity Assisted Ion Beam

Qian Bi, Zhili Chen *, Yuzhao Liu, Li Tang, Yingxue Xi and Weiguo Liu

Shaanxi Province Key Laboratory of Thin Film Technology and Optical Test,
School of Photoelectric Engineering, Xi'an Technological University, Xi'an 710021, China;
stubi@163.com (Q.B.); lyz941328@163.com (Y.L.); opstang@163.com (L.T.);
xiyingxue@163.com (Y.X.); wgliu@163.com (W.L.)

* Correspondence: chenzhili@xatu.edu.cn

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Abstract: The metal impurity assisted ion beam technology has shown its uniqueness and effectiveness in the formation and precise control of nanostructures on the surface of materials. Hence, the investigation in this area is vital. The morphology evolution of self-organized nanostructures induced by Fe co-deposition assisted Ar⁺ ion beam sputtering at a different distance from the impurity target was investigated on sapphire, using atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). We also investigated the role of metal impurities on sapphire ripple formation. Experiments were carried out at an oblique angle of incidence 65° with constant ion beam current density 487 $\mu\text{A}/\text{cm}^2$ and the erosion duration of 60 min at room temperature (20 °C). The introduction of Fe impurity increased the longitudinal height and roughness of the surface nanostructures. Moreover, the amounts of Fe deposited on the surface decreased with increasing distance, and the morphology of the smooth sapphire surface demonstrated a strong distance dependence. Differences in surface morphology were attributed to changes in metal impurity concentration. With an increase of impurity target distance, island-like structures gradually evolved into continuous ripples. At the same time, the orderliness of nanostructures was enhanced, the longitudinal height gradually decreased, while the spatial frequency was unchanged. In addition, there were very few metal impurities on the etched sample. During the ion beam sputtering process, island-like structures promoted the growth of ripples but destroyed their orderliness.

Keywords: self-organized nanostructure; surface morphology; root-mean-square roughness (RMS); sapphire; ion beam; atomic force microscope (AFM)

1. Introduction

Metal impurity assisted ion beam as an effective means can not only control the growth of self-organized nanostructures but modulate nanopatterns too [1–3]. For instance, introducing metal impurities will promote the formation of patterns below the critical incidence angle of the ion beam, improve the orderliness and modulate the symmetry, etc. This technology can be applied in microelectronic device manufacturing, catalysis, nanomagnetism, plasma electronics, and so on. The surface structures can be artificially controllable by adjusting the introduction of metal impurity atoms, which may compensate for the defects of the pure ion beam sputtering (IBS). Therefore, the investigation and exploration of metal impurity-assisted ion beam induced nanostructures are significant.

To date, researchers have used Ar⁺, Kr⁺, and other gases ions to etch the surface of Si-doped with metal ions such as Fe, Mo, and stainless steel (SS) to prepare nanostructures [4–8]. Dekang Chen of

the University of science and technology of China observed well-ordered ripple structures for the co-deposition of Mo atoms during Ar⁺ bombardment [9]. These patterns present with a particular anti-reflection property in the ultraviolet band. Ying Liu et al. also observed the novel surface nanopatterning of pre-striated quartz irradiated with Ar⁺ ions under concurrent Aluminum (Al) impurity co-deposition, which provided an essential reference in optical applications [10]. Bhowmik et al. prepared good periodic ripple patterns on the surface of Si by non-pure Ar ion beam bombardment, and found that the pollutants in the ion beam played a significant role in the formation of ripple patterns [11].

At present, there are no extensive reports on metal impurity assisted ion beam induced nanostructures in domestic and foreign scientific institutes and universities. The previous investigations on the preparation of nanostructures have mainly focused on semiconductor materials [12–19], and few studies have been conducted on optical materials [20]. Moreover, the internal physical mechanism has not yet been elucidated, limiting the application and development of this technology in nanofabrication.

Sapphire is a typical and widely available compound of Aluminum that contains only Al and oxygen. Due to excellent mechanical, optical, chemical, electrical, and anti-radiation properties, it is widely used in military, civil, and scientific research, such as the optical system, special window, infrared guidance, etc. [21]. To date, there is no report on the Ar ion irradiation of sapphire with Fe co-deposition. Introducing well-ordered structures into the surface of the sapphire crystal, the crystal can effectively exert its characteristics, e.g., obtaining high transmittance, high intensity, and high imaging quality.

At present, it is common to conduct distance evolution experiments in the related investigation of impurity co-deposition. Still, there is a limitation in that most of the experimental materials are semiconductor materials such as silicon, and there is almost no investigation of optical materials such as sapphire. Therefore, the distance evolution experiment conducted in this paper will make up for the above limitation: using sapphire as the erosion material in order to lay the foundation for the subsequent study of the optical properties of its structure. The distance between the sapphire sample and the impurity target can be adjusted under oblique incidence to investigate the evolution of the surface nanostructures of the etched sapphire sample. According to the current investigations on sapphire, the better the orderliness of the nanostructures and the higher the longitudinal height, the higher the transmittance of the sapphire, and to a certain extent, the sapphire crystal will have an anti-reflection effect. Therefore, we expect to prepare high-aspect-ratio and well-ordered dot, column, and ripple nanostructures on the sapphire surface. Moreover, it is hoped that fewer metal impurities remain on the surface of the etched sapphire. In this article, we have investigated the pattern formation on sapphire irradiated by 1000 eV Ar ion beam with Fe co-deposition and without Fe co-deposition, and explored the role of metal impurities on sapphire ripple formation. Meanwhile, the morphology evolution of self-organized nanostructures induced by Ar⁺ ion beam sputtering Fe co-deposition at a different distance from the impurity target was investigated on sapphire. In summary, our work provides some explanations for the evolution of intricate patterns on the sapphire surface and also provides an essential reference for the further study of self-organized nanostructures.

2. Materials and Methods

Double-sided polished sapphire (C-direction) samples were bombarded with 1000 eV Ar ion at oblique incidence in a vacuum chamber with a base and working pressure of 2×10^{-3} Pa and 2.5×10^{-2} Pa, respectively. The ion beam was extracted from a self-made microwave cyclotron resonance ion source with a diameter of 120 mm at room temperature under the premise of ultra-high purity (99.999%) Ar gas. The schematic diagram of the microwave cyclotron resonance ion source is shown in Figure 1.

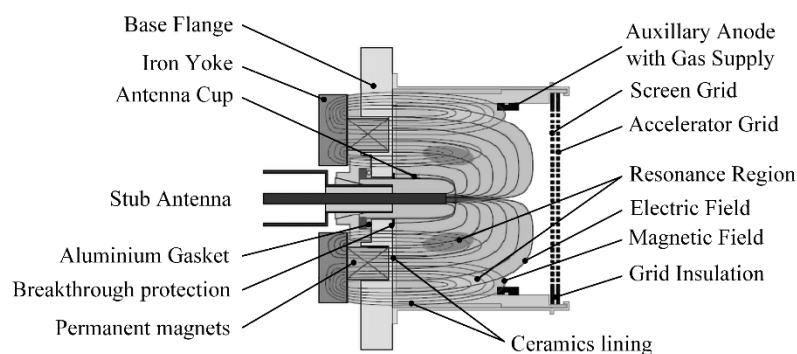


Figure 1. Schematic diagram of microwave cyclotron resonance ion source.

A Fe target was used with a height of 8.66 mm, a thickness of 1 mm, and a length of 30 mm. The schematic diagram of the impurity target is shown in Figure 2. Here, A, B, C, and D respectively represent the position of the sample in the impurity target, and the interval is 10 mm. The black arrows in the figure indicate the incident direction of the ion beam.

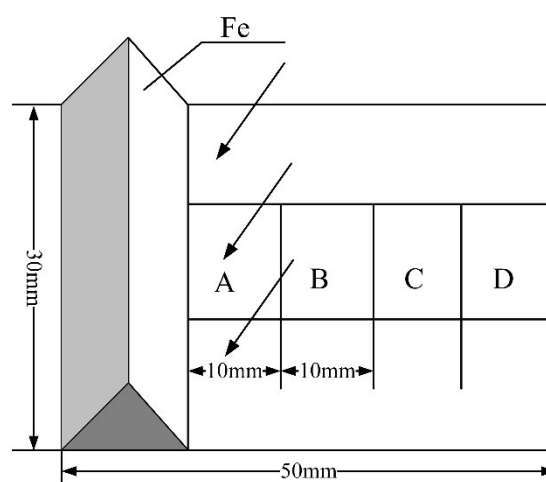


Figure 2. Impurity target structure: ridge structure.

The irradiation was carried out in two different ways, one with Fe co-deposition and another without Fe co-deposition. All samples did not rotate. The ion beam incident angle was fixed at 65° with a bombardment duration of 60 min, corresponding to a beam density of approximately $487 \mu\text{A}/\text{cm}^2$. During ion beam bombardment, Fe target and sapphire samples were sputtered at the same time. All substrates were bombarded by IBS with a simultaneous Fe co-deposition at room temperature (20°C). To investigate the morphology evolution of self-organized nanostructures induced by distance, additional samples were positioned at a different target distance from 1 cm to 4 cm at the same experimental parameters. The target distance is the space between substrates and the impurity target.

The surface topography was characterized by an atomic force microscope (AFM, Bruker, Billerica, MA, USA); the root mean square roughness (RMS) was measured by the non-contact surface measuring instrument (Taylor Surf CCI2000, Berwyn, PA, USA) was used to measure the roughness; the orderliness of nanostructures was observed by the power spectral density (PSD). X-ray photoelectron spectroscopy (XPS, Thermo VG, Scientific, ESCALAB 250, Waltham, MA, USA) was performed to obtain chemical information on samples.

3. Theory

The Bradley-Harper model (BH model) is based on the Sigmund sputtering theory [22], which describes the physical mechanism of the formation of self-organized nanostructures on amorphous

solid surfaces by ion beam etching. The BH model believes that the sputtering rate is different due to the difference in the sputtering yield of the atoms located in different curvature of the solid surface, so the modulated self-organized nanostructures appear on the solid surface. Further, it is believed that the sputtering rate of the concave position on the solid surface is greater than that of the convex position. Bradley and Harper derived the linear equation of surface morphology evolution:

$$\frac{\partial h}{\partial t} = -v_0 + v_x \frac{\partial^2 h}{\partial x^2} + v_y \frac{\partial^2 h}{\partial y^2} + K \nabla^4 h + \eta(x, y, t) \quad (1)$$

where: v_0 is the erosion velocity of a flat surface, and K is the relaxation rate caused by surface diffusion; $\eta(x, y, t)$ is Gaussian random noise; v_x, v_y is the effective surface tension generated during the etching process, which is related to the ion incident angle.

After amounts of experimental research and quantitative analysis of the model, scholars found that, during the ion beam sputtering process, there is not only the smoothing mechanism of surface thermal diffusion, but the surface viscous flow is also a crucial factor, which affects the smoothing mechanism, and plays an essential role in the formation of surface nanostructures.

Surface viscous flow refers to the fluid movement of atoms on the solid surface due to the existence of pressure difference, which appears on the surface of amorphous materials [23]. The mathematical expression is as follows:

$$\frac{\partial h}{\partial t} = -J\Omega \frac{\gamma \Delta^3}{\eta_r} \nabla^4 h \quad (2)$$

where Δ is the thickness of the surface layer with the viscous flow, and η_r is the viscosity coefficient; γ is the surface energy; Ω is the atomic volume.

With the addition of the surface viscous flow factor, the modified BH model can be expressed as follows:

$$\frac{\partial h}{\partial t} = -v_0 + v_x \frac{\partial^2 h}{\partial x^2} + v_y \frac{\partial^2 h}{\partial y^2} + \left(J\Omega \frac{\gamma \Delta^3}{\eta_r} + K \right) \nabla^4 h + \eta(x, y, t) \quad (3)$$

where $v_0 = \frac{JY_0(\theta)}{n}$ is the sputtering rate of an approximately smooth plane under ion beam sputtering, $Y_0(\theta)$ is the sputtering yield of a smooth plane when the incident angle of the ion beam is θ , which can be expressed as:

$$Y_0(\theta) = \frac{\Lambda \varepsilon n \rho}{\sqrt{2\pi} \alpha \beta} \exp\left(-\frac{\rho^2}{2\alpha^2}\right) B_1^{-\frac{1}{2}}(\theta) \exp\left(\frac{A^2(\theta)}{2B_1(\theta)}\right) \quad (4)$$

where ε is the total energy deposited on the surface of the material, ρ is the average depth of ion penetration, α and β is the distribution width parallel and perpendicular to the ion direction, and n is the number of atoms per unit volume. $\Lambda = \left(3/4\pi^2 n_v u_0 c_0\right)$, where n_v is the density of atoms, u_0 is the binding energy of atoms on the surface of the material, c_0 is a constant of proportionality, and A and B_1 are only related to α, β, θ .

After introducing Fe impurity, Fe atoms will prevent the deposition of Ar ions on the sapphire surface, which reduces the depositing depth of Ar ions under the sapphire surface, i.e., ρ in Equation (4) decreases, as $Y_0(\theta)$ also decreases. The heat flow effect of the sapphire material is proportional to the energy deposited by the ion beam. Fe impurities weaken the ion beam deposition on the sapphire surface, resulting in a weakening of the heat flow effect of the material, i.e., the thickness of the surface cladding layer with the viscous flow is smaller, then Δ in Equation (3) decreases and $Y_0(\theta)$ decreases. Therefore, according to the preferential sputtering theory, the existence of Fe impurities will lead to a decrease in sputtering yield at the impurity deposition region. A schematic diagram of preferential sputtering theory is presented in Figure 3. Where there is no Fe deposition area, the sputtering yield does not interfere. This difference in sputtering yield makes the sapphire surface easy to produce high-depth nanostructures.

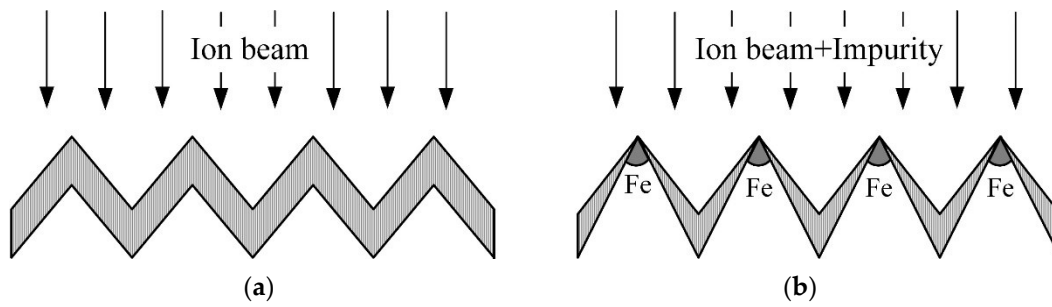


Figure 3. Schematic diagram of preferential sputtering theory. (a) Schematic diagram of pure ion beam sputtering; (b) Schematic diagram of impurity co-deposition ion beam sputtering.

The concentration of metal impurities is directly proportional to the target distance. That is, the concentration of metal impurities will decrease as the target distance increases. which is

$$c \propto \frac{1}{d} \quad (5)$$

where c is the concentration of metal impurities, and d is the target distance. When the target distance is very far, the impurities concentration is small, so the sapphire surface tends to be sputtered without Fe impurities. When the sapphire surface without impurities sputtered by Ar ion beam, the surface mostly appears ripple nanostructures, where

$$p_1 \propto d \quad (6)$$

where p_1 is the occurrence probability of the ripple structure. When impurities are introduced, island-like structures appear on the surface of sapphire, and the occurrence probability of island-like structures is proportional to the impurity concentration, and

$$p_2 \propto c \quad (7)$$

where p_2 is the occurrence probability of island-like structure, combined with Equation (5), we can get

$$p_2 \propto \frac{1}{d} \quad (8)$$

Therefore, it can be predicted that when the target distance is small, the nanostructures formed on the sapphire surface are mainly island-like structures. When the target distance is quite large, mostly ripple nanostructures are formed on the sapphire surface.

4. Results

To study the impact of metal impurity on nanopatterning formation on the surface of sapphire, experiments were conducted with Fe co-deposition and without Fe co-deposition by Ar ion beam sputtering at room temperature (20 °C). Patterns were prepared by sputtering for 60 min with a bombardment energy 1000 eV at an incidence angle of 65°, and samples did not rotate. We also used sapphire samples to investigate the effects of the distance on the topography evolution with simultaneous Fe co-deposition at the same experimental condition.

4.1. Dependence of Nanostructures on the Introduction of Metal Impurity

Figure 4 shows the surface morphologies of substrates after being bombarded by the Ar^+ ion beam with Fe co-deposition and without Fe co-deposition. Experiments were conducted at an incidence angle of 65° corresponding to a beam density of approximately $487 \mu\text{A}/\text{cm}^2$ and with a bombardment energy 1000 eV and duration of 60 min at room temperature (20°C). The small figures in the bottom right corner of the picture show the Fourier spectrum of the AFM measurement results. The scanning range of the image is $2 \mu\text{m} \times 2 \mu\text{m}$, Z is the longitudinal height of the nanostructures. Figure 5 presents the PSD curve diagram of the nanostructures formed on the surface, denoting the orderliness of the nanostructures.

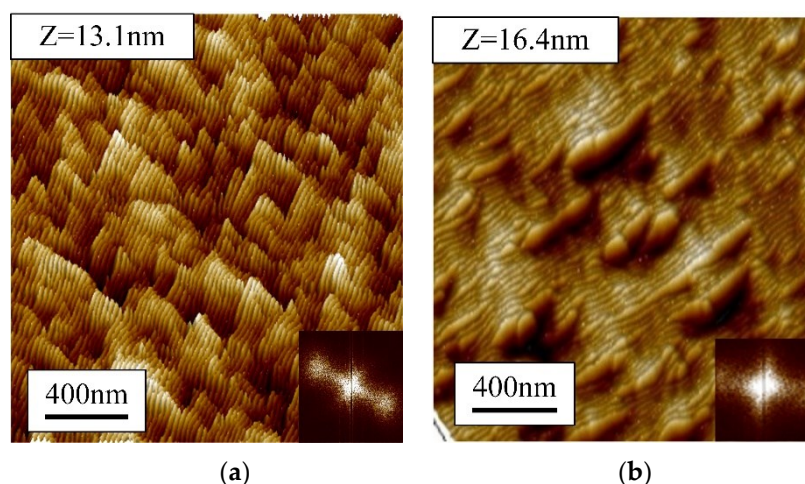


Figure 4. AFM topography of sapphire sputtered with or without Fe assisted Ar ion beam, at an incident angle 65° , incident energy 1000 eV, beam density $487 \mu\text{A}/\text{cm}^2$, duration time 60 min. (a) patterns bombarded with a pure ion beam (b) patterns bombarded with simultaneous Fe co-deposition and taken at a position 2 cm from the Fe target. Top-left and bottom-right insets show the corresponding longitudinal height and Fourier transform, respectively.

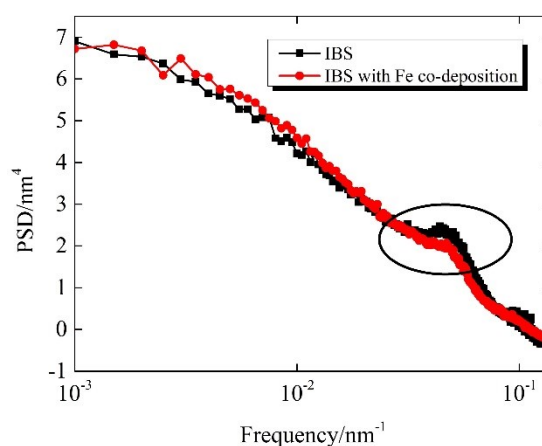


Figure 5. PSD of sapphire after 1000 eV Ar^+ bombardment at a fixed incidence angles 65° , with beam density $487 \mu\text{A}/\text{cm}^2$. (a) patterns bombarded with a pure ion beam (b) patterns bombarded with simultaneous Fe co-deposition and taken at a position 2 cm from the Fe target.

The experimental results in Figures 4 and 5 show that: There are obvious differences between the self-organized nanostructures formed by introducing metal impurities-assisted Ar^+ ion beam sputtering sapphire sample surface and the non-impurity-assisted Ar ion beam sputtering sapphire sample surface.

When the sapphire surface is sputtered with a pure Ar^+ ion beam, ripple nanostructures are formed on the sample surface. The longitudinal height of the nanostructures is 13.1 nm, and the

roughness is 1.9 nm. A highly symmetrical point appears in the Fourier spectrogram. And pronounced characteristic peaks are observed in the PSD graph, which indicates ripple nanostructures formed on the surface are highly ordered.

When the sapphire surface is bombarded by Ar^+ ion beam with Fe co-deposition, the surface of the sample formed mixed nanostructures, i.e., island structures and ripple structures. The longitudinal height of the nanostructure is 16.4 nm, the roughness is 2.29 nm, and symmetry points appear in the Fourier spectrogram. And relatively prominent characteristic peaks are also observed in the PSD curve, so the nanostructures formed on the surface are relatively well ordered.

Compared with pure ion beam irradiation, after the introduction of Fe impurities, obvious island-like structures will be formed on the sapphire surface. The longitudinal height of the nanostructures and RMS increased with the introduction of Fe impurity.

4.2. Dependence of Nanostructures on the Distance of Metal Impurity Target

Figure 6a–d show the AFM images taken at some particular positions X_i with $i = 1, 2, 3, 4$ mm from the Fe target of sapphire substrate irradiated at the same condition. The small figures in the bottom right corner of the picture show the Fourier spectrum of the AFM measurement results. The scanning range of the image is $2 \mu\text{m} \times 2 \mu\text{m}$, Z is the longitudinal height of the nanostructures.

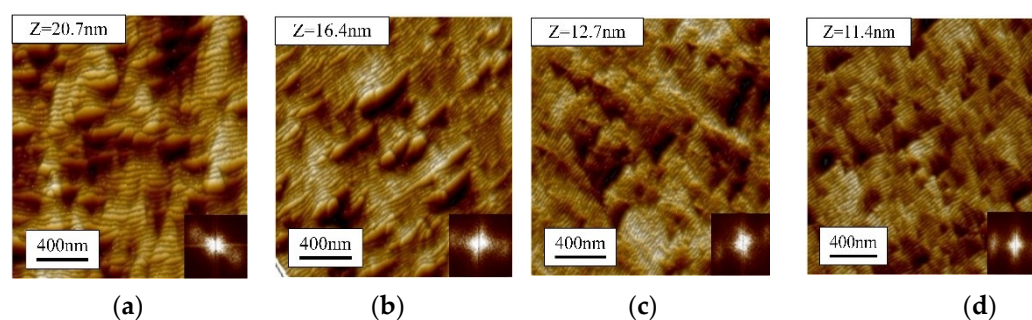


Figure 6. Typical AFM images ($2 \mu\text{m} \times 2 \mu\text{m}$) of post irradiated sapphire samples with Fe co-deposition at distances from the Fe target of (a) 1 cm, (b) 2 cm, (c) 3 cm, (d) 4 cm, at an oblique angle of incidence 65° with constant ion beam current density $487 \mu\text{A}/\text{cm}^2$ and the erosion duration of 60 min. Top-left and bottom-right insets show the corresponding longitudinal height and Fourier transform, respectively.

The experimental results shown in Figures 6 and 7 indicate that the morphology of the nanostructures has a pronounced evolution with the change of the distance. It can be roughly divided into three regions according to the discrepancy of nanostructures, as described in the following.

Near target region (1 cm): Both islands and ripples pattern coexist on substrates, with a longitudinal height of 20.7 nm, and from the Fourier spectrum, the characteristic peak is not observed. The surface roughness of the sample is 2.9 nm. The characteristic peak is not evident in the PSD curve, which means that the orderliness of the nanostructures is relatively low.

Middle region (2 cm): The density of the island-like structures decreases, the longitudinal height is reduced to 16.4 nm, and symmetry points appear in the Fourier spectrum. A relatively visible characteristic peak is observed from the PSD curve, with relatively ordered patterns form on the sample surface, and the surface roughness reduces to 2.29 nm.

Far target region (3 cm–4 cm): The longitudinal height of nanopatterns continues to decrease with the formation of fined ripple patterns on the sample surface. And the prominent characteristic peak appears in the Fourier spectrum. The surface roughness continues to decrease. The notable characteristic peak is observed from the PSD curve, and well-ordered ripple nanostructures appear on the surface of the sample.

In this case, with increasing distance, the surface roughness of the morphologies decreases, which shows the correlation between RMS and the distance from the impurity target.

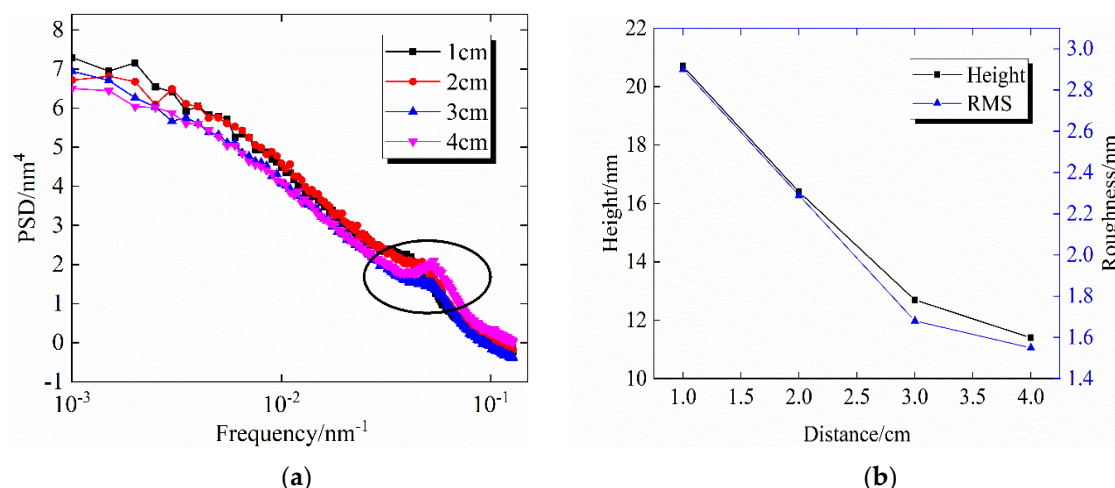


Figure 7. Curves of PSD, RMS, and Height of the sample surface with the distance of impurity target. (a) PSD curve; (b) RMS, Height curve.

The chemical composition of the sample surface is characterized by XPS is shown in Figure 8. Samples have been analyzed at a distance of 1 cm and 4 cm away from the Fe target during ion bombardment, respectively. And there is no pronounced Fe peak in Figure 8. Through the integration of XPS peaks, the atomic amount of the main elements in the sample is estimated. The concentration of the Fe atoms in the near target region (1 cm) is 0.45%, and in the far target area (4 cm) is 0.09%. It indicates that few metal impurities are remaining on the surface of the samples and clearly shows the difference between the near target area and the far target area: the metal impurity concentration of the near target area is more than the far target area. With increasing distance from the Fe target, the metal impurity content gradually decreases.

Combined with Figure 6, the longitudinal height of the nanostructures in the near target region is also higher than the far target region. It is evident that: differences in metal impurity concentration during the ion bombardment cause the discrepancy in the surface structures, i.e., differences in metal impurity concentration promote the evolution of nanostructures.

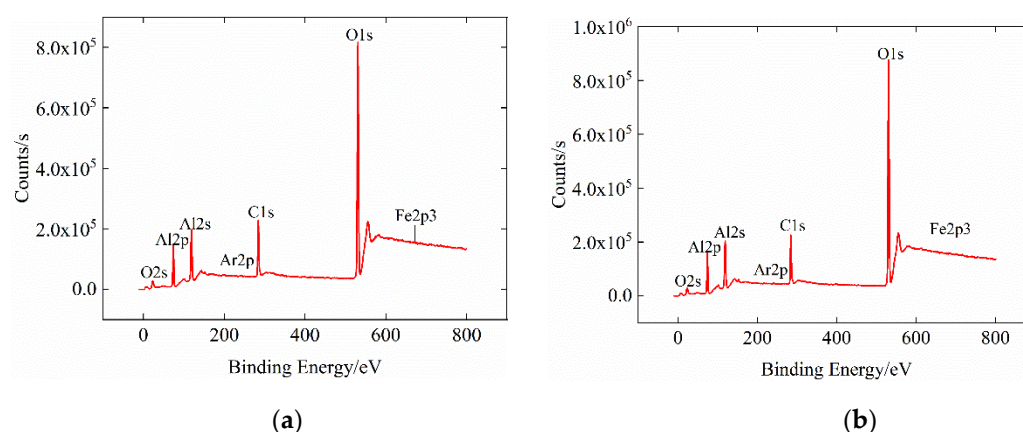


Figure 8. XPS spectrum of the Fe co-deposition irradiated samples surface. (a) XPS spectrum of the near target region; (b) XPS spectrum of the far target region.

5. Discussion

5.1. Effect of the Introduction of Impurity on the Morphology of Nanostructures

In the initial stage of ion beam sputtering, incident ions enter the substrate to a certain depth and transfer their energy to the surrounding substrate atoms. These substrate atoms with sufficient energy break the bondage and sputter, then leave their original position. In this process, the sputtered atoms will condense on the surface of the substrate. Due to surface diffusion and surface dynamics restriction, the atoms tend to form small and mobile clusters on the surface of the substrate to nucleate. When these atomic groups are smaller than the critical nucleation size, they may disappear or grow. On the contrary, when they are larger than the critical nucleation size, they will accept new atoms and gradually increase to form island-like structures. With the introduction of Fe atoms, the surface becomes rougher.

The experimental results show that the longitudinal height and roughness of the nanostructures on the surface of the sapphire with Fe impurities are significantly higher than the body without impurities. And the orderliness of nanostructures was affected by the introduction of metal impurity. According to the BH model theory, due to the different local curvatures of the samples and different sputtering yields, the top etching rate is lower than the bottom etching rate. With the advancement of the etching process, the difference between the top and bottom becomes larger and larger, which promotes the growth of nanostructures, and increases the longitudinal height of the nanostructures. In a word, impurities have a significant impact on the morphology of nanostructures.

5.2. Effect of Impurity Target Distance on the Morphology of Nanostructures

From the analysis of the above experimental results, the closer to the Fe target, the higher the density of the island-like structures. As the distance gets farther, the island-like structures gradually disappear, and substrates appear relatively ordered ripple nanostructures. According to the theory of surface activated sputtering, when impurities deposit on the surface of sapphire, a stable and uniform layer will be formed on the body. That is a mixture of Fe and sapphire. Metal impurity atoms change the sputtering yield (growth effect) and surface diffusion (smoothing effect) properties of the atoms in the surface covering layer. Moreover, they affect the strength of the surface growth mechanism and surface smoothing mechanism during the ion beam irradiation.

During the irradiation process, the introduction of metal impurity atoms activates the sputtering properties of the solid surface. At the same time, due to the increase of the distance between the sample and the metal target, the metal impurities deposit unevenly on the sample surface, resulting in the island-like structures gradually evolve into continuous ripple nanostructures. Thus, as the distance increases, the irradiated surface develops from initially mixed morphology (island-like structures and ripples), gradually to a fined structure morphology.

5.3. Effect of the Change of Impurity Target Distance on the Characteristic Wavelength of Nanostructures

As shown in Figure 7a, the positions of the characteristic peaks of the nanostructures PSD curves corresponding to different target distances are almost the same, which indicates that the characteristic wavelength of the formed surface structures is unchanged. During the ion beam sputtering process, the interaction between the ion beam etching mechanism and the smoothing mechanism develop periodic structures. The BH model theory stipulates that the surface smoothing mechanism is caused by thermal diffusion. At high temperatures, the change in the incident angle is the main reason for the characteristic wavelength change of the nanostructures. In this experiment, the incident angle of the ion beam is fixed at 65°, and the results show that the characteristic wavelength corresponding to different target distances is unchanged. Therefore, during the ion beam irradiation, the change of the target distance does not affect the characteristic wavelength of the nanostructures.

5.4. Effect of Impurity Target Distance on the Orderliness of Nanostructures

Figure 6 shows the relationship between pattern formation and space: near the target region, ripples, and island-like nanostructures generate on the surface of the sample. The longitudinal height of the nanostructures is relatively higher. Meanwhile, the characteristic peak in the PSD curve is not pronounced, which indicates that nanostructures are somewhat disordered. Instead, in the far target region, ripple nanostructures with a relatively lower longitudinal height appear on the surface of the sample. Moreover, the PSD curve shows a pronounced characteristic peak with well-ordered nanostructures generate on the surface of substrates. However, when there is no impurity target, ion beam sputtering is performed under the same ion beam parameters, and the nanostructures on the sample surface at any position is consistent. Therefore, when the impurity target exists, the formation of nanostructures on the sample surface at different distances is closely related to the concentration of metal impurities.

When the sample is very close to the metal impurity target, the concentration of metal impurities deposits on the surface of the substrates is higher. The probability of metal impurities deposit on the island structures increases and forms a protective layer on top of the island structures. The protective layer reduces the sputtering rate on the top of the island structure, which causes the sputtering rate at the bottom of the island structure to be faster than the top so that the height of nanostructures increases. During the sputtering process, island-like structures are continuously produced, and its density is growing continually. Then a new fine structure is created, as shown in Figure 9. These novel delicate structures destroy the orderliness of the surface nanostructures. Compared with the initial nanostructures, the novel nanostructures possess petite longitudinal height and lateral dimensions. Therefore, these delicate structures will only affect the orderliness of the surface nanostructures but have no effect on the characteristic wavelength of nanostructures. When the distance from the metal impurity target is getting farther, the concentration of the metal impurity deposit on the surface of the sample decreases, and the probability of deposition on the island structure becomes lower. Then, the density of the island-like structures declines, the height of the pattern decreases, but the orderliness gradually increases. Therefore, the farther away from the impurity target, the better the orderliness of the nanostructures.

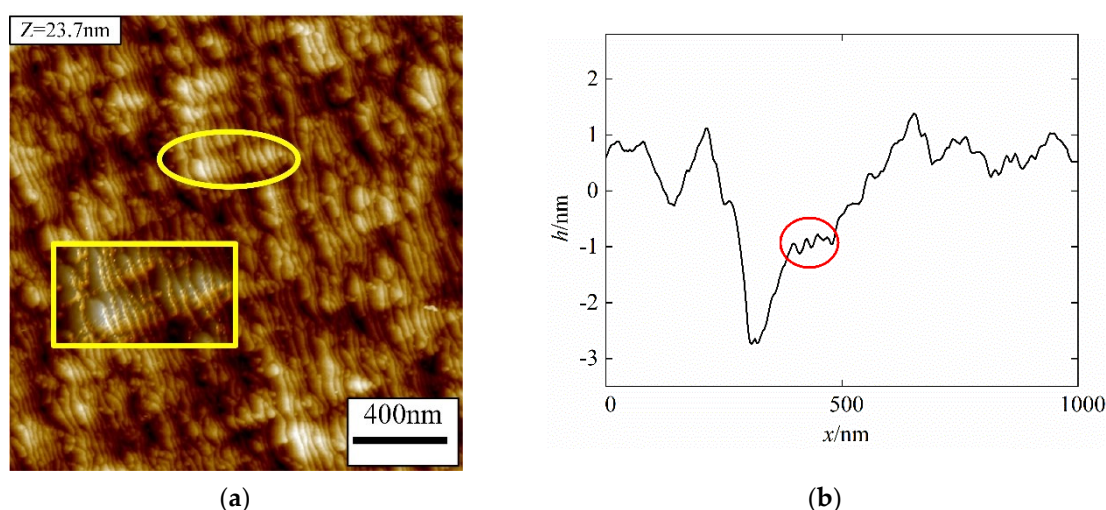


Figure 9. The surface morphology of the sample near the target area. (a) Island-like structures of the surface; (b) Sectional view of the island-like structures.

6. Conclusions

In this report, we have investigated the role of metal impurity during the bombardment and studied the morphology evolution of Ar^+ ion beam sputtering sapphire assisted with Fe co-deposition and analyzed the mechanism of pattern formation on sapphire. It is found that the longitudinal height and roughness of the nanostructures are increased by introducing metal impurity. Moreover, the

introduction of such an impurity affects the orderliness of nanostructures. The chemical state change of Fe_{2p} peak by increasing the distance from the impurity target will be analyzed and checked in future work. XPS is mainly used to analyze the kinds of impurity elements remaining on the etched sapphire surface and to compare the changes in the concentration of the primary metal impurity elements with distance in this work. The experiment results show that fewer metal impurities remain in the etched sapphire surface. We also found that the longitudinal height and roughness of nanopatterns decrease with an increase in distance. However, the orderliness of the nanostructures gradually enhances with the increased space. Further, the wavelength (spatial frequency) remains unchanged. The difference in metal impurity concentration promotes the evolution of nanostructures. In other words, the discrepancy in nanostructures is attributed to the difference in concentration of metal impurities. As a result, pattern formation during sputter erosion is strongly influenced by distances, which leads to a wide variety of novel surface morphologies on the nanoscale.

In this technology, the characteristics of self-organized patterns can be easily controlled by adjusting the distance between the impurity target and the substrate. Further, high-aspect-ratio, well-ordered nanostructures can be quickly obtained. These results provide some explanations for the evolution of intricate patterns on the sapphire surface and provide a valid basis and reference for the manufacture of sapphire nanostructures.

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References

1. Chen, D.; Yang, G.; Li, J.; Hirsch, D.; Liu, Y.; Frost, F.; Hong, Y. Terrace morphology on fused silica surfaces by Ar⁺ ion bombardment with Mo co-deposition. *Appl. Phys. Lett.* **2018**, *113*, 033102, doi:10.1063/1.5039565.
2. Cornejo, M.; Ziberi, B.; Meinecke, C.; Hirsch, D.; Gerlach, J.W.; Höche, T.; Frost, F.; Rauschenbach, B. Self-organized patterning on Si(001) by ion sputtering with simultaneous metal incorporation. *Appl. Phys. A* **2011**, *102*, 593–599, doi:10.1007/s00339-011-6246-y.
3. Gago, R.; Jaafar, M.; Palomares, F.J.; Simon, F.J.P. Surface morphology of molybdenum silicide films upon low-energy ion beam sputtering. *J. Phys. Condens. Matter* **2018**, *30*, 264003, doi:10.1088/1361-648x/aac4f6.
4. Vayalil, S.K.; Gupta, A.; Roth, S.V.; Ganesan, V. Investigation of the mechanism of impurity assisted nanoripple formation on Si induced by low energy ion beam erosion. *J. Appl. Phys.* **2015**, *117*, 024309, doi:10.1063/1.4905684.
5. Vayalil, S.K.; Gupta, A.; Roth, S.V. Study of pattern transition in nanopatterned Si(100) produced by impurity-assisted low-energy ion-beam erosion. *Appl. Phys. A* **2017**, *123*, 224006, doi:10.1007/s00339-017-0756-1.
6. Lloyd, K.S.; Bolotin, I.L.; Schmeling, M.; Hanley, L.; Veryovkin, I.V. Metal impurity-assisted formation of nanocone arrays on Si by low energy ion-beam irradiation. *Surf. Sci.* **2016**, *652*, 334–343, doi:10.1016/j.susc.2016.03.016.
7. Khanbabaee, B.; Lützenkirchen-Hecht, D.; Hübner, R.; Grenzer, J.; Facsko, S.; Pietsch, U. Near surface silicide formation after off-normal Fe-implantation of Si(001) surfaces. *J. Appl. Phys.* **2014**, *116*, 024301, doi:10.1063/1.4887516.
8. Zhang, K.; Bobes, O.; Hofsäss, H. Designing self-organized nanopatterns on Si by ion irradiation and metal co-deposition. *Nanotechnology* **2014**, *25*, 085301, doi:10.1088/0957-4484/25/8/085301.
9. Chen, D. *Self-Organized Nanostructures on SiO₂ Surface Induced by Low-Energy Ion Bombardment at Oblique Incidence with Impurity Co-Deposition*; University of Science and Technology of China: Hefei, China, 2019.

10. Liu, Y.; Hirsch, D.; Fechner, R.; Hong, Y.; Fu, S.; Frost, F.; Rauschenbach, B. Nanostructures on fused silica surfaces produced by ion beam sputtering with Al co-deposition. *Appl. Phys. A* **2017**, *124*, 73, doi:10.1007/s00339-017-1393-4.
11. Bhowmik, D.; Mukherjee, M.; Karmakar, P. Presence of reactive impurities in Ar⁺ ion beam plays a key role for Si ripple formation. *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At.* **2019**, *444*, 54–61, doi:10.1016/j.nimb.2019.02.010.
12. Hernandez, A.; Kudriavtsev, Y.; Gallardo, S.; Avendaño, M.; Asomoza, R. Formation of self-organized nano-surfaces on III–V semiconductors by low energy oxygen ion bombardment. *Mater. Sci. Semicond. Process.* **2015**, *37*, 190–198, doi:10.1016/j.mssp.2015.02.074.
13. Bradley, R.M. Morphological transitions in nanoscale patterns produced by concurrent ion sputtering and impurity co-deposition. *J. Appl. Phys.* **2016**, *119*, 134305, doi:10.1063/1.4945678.
14. Moon, B.; Yoo, S.; Kim, J.-S.; Kang, S.J.; Muñoz-García, J.; Cuerno, R. Ion-beam nanopatterning of silicon surfaces under codeposition of non-silicide-forming impurities. *Phys. Rev. B* **2016**, *93*, doi:10.1103/physrevb.93.115430.
15. Chowdhury, D.; Satpati, B.; Ghose, D. Temperature and high fluence induced ripple rotation on Si(100) surface. *Mater. Res. Express* **2016**, *3*, 125003, doi:10.1088/2053-1591/3/12/125003.
16. Bhattacharjee, S.; Lavanyakumar, D.; Naik, V.; Mondal, S.; Bhattacharyya, S.; Karmakar, P. Nanomechanical properties of ion induced Si ripple patterns. *Thin Solid Film.* **2018**, *645*, 265–268, doi:10.1016/j.tsf.2017.10.053.
17. Novakowski, T.J.; Tripathi, J.; Hassanein, A. Silicon nanocone formation via low-energy helium ion sputtering. *J. Vac. Sci. Technol. B* **2018**, *36*, 051202, doi:10.1116/1.5040765.
18. Bhowmik, D.; Karmakar, P. Energy dependent ripple growth on Si(100) by N⁺ ion beam irradiation. *AIP Conf. Proc.* **2017**, *1832*, 80019, doi:10.1063/1.4980479.
19. Chen, Z.; Liu, W.; Zhang, J.; Wang, M. Nano Pyramid Microstructures on Ag Film Induced by Low Energy Ion Beams. *Acta Photonica Sin.* **2014**, *43*, 116003, doi:10.3788/gzxb20144301.0116003.
20. Chen, Z.; Liu, W.; Yang, L. Self-Organizing Nano-Structure and Optical Properties of Sapphire Induced by Low Energy Ion Beam. *Chin. J. Lasers* **2015**, *42*, 0306003, doi:10.3788/cjl201542.0306003.
21. Fei, M.; Chen, Z.; Liu, W. Experimental Research on Sapphire Crystal Induced by Low Energy Kr⁺ Ion Beam. *Acta Photonica Sin.* **2019**, *48*, 143–148.
22. Sigmund, P. Mechanisms and theory of physical sputtering by particle impact. *Nucl. Instrum. Methods Phys. Res.* **1987**, *27*, 1–20, doi:10.1016/0168-583X(87)90004-8.
23. Harrison, M.P.; Pearson, D.A.; Bradley, R.M. Emergence and detailed structure of terraced surfaces produced by oblique-incidence ion sputtering. *Phys. Rev. E* **2017**, *96*, 032804, doi:10.1103/PhysRevE.96.032804.

