Characterization of zirconium thin films deposited by pulsed laser deposition*

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Zirconium (Zr) thin films deposited on Si (100) by pulsed laser deposition (PLD) at different pulse repetition rates are investigated. The deposited Zr films exhibit a polycrystalline structure, and the X-ray diffraction (XRD) patterns of the films show the α Zr phase. Due to the morphology variation of the target and the laser–plasma interaction, the deposition rate significantly decreases from 0.0431 Å/pulse at 2 Hz to 0.0189 Å/pulse at 20 Hz. The presence of droplets on the surface of the deposited film, which is one of the main disadvantages of the PLD, is observed at various pulse repetition rates. Statistical results show that the dimension and the density of the droplets increase with an increasing pulse repetition rate. We find that the source of droplets is the liquid layer formed under the target surface. The dense nanoparticles covered on the film surface are observed through atomic force microscopy (AFM). The root mean square (RMS) roughness caused by valleys and islands on the film surface initially increases and then decreases with the increasing pulse repetition rate. The results of our investigation will be useful to optimize the synthesis conditions of the Zr films.

Keywords: laser processing, Zr thin film, droplet, pulse repetition rate

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1. Introduction

Zirconium has attracted considerable attention in many application fields, such as the nuclear industry, reprocessing plants, and material science, because of its low thermal neutron cross-section, exceptional corrosion resistance under high temperature and high pressure, and excellent hydrogen storage property.[1–4] Over the past few decades, the structural and physical properties of bulk Zr and its alloys have been widely investigated.[5–7] Many deposition methods are used to obtain Zr thin films with various properties, including special ω phase,[8,9] outstanding microstructures, and mechanical properties.[10,11] Polycrystalline Zr films are used in various applications, such as thin multilayers with higher coercivity.[12] Compared to the bulk materials, the pretty unique properties of the films, such as a high surface area, compact structure, and small size, make them excellent hydrogen storage materials.[13]

Pulsed laser deposition (PLD) is commonly used to deposit various materials. In contrast to other techniques, the PLD can be performed at a relatively low temperature and yield high-purity films with promising physical and structural properties at the nanoscale.[14–17] However, one of the main disadvantages of the PLD is the presence of droplets on the surfaces of the deposited films. The droplets are inevitably formed in a complex physical process during target ablation and plasma plume expansion. The physical process is affected by the laser parameters and experimental conditions.[17–23] The presence of droplets could affect the physical properties and the potential applications of the films. Great efforts have been taken to reduce the size and the density of the droplets that cover on the surfaces of the as-deposited films. The influence of the laser fluence on the presence of droplets has been investigated by many researchers.[15,21–23] Some other investigators focus on the relationship between the target morphology and the droplet due to the laser ablation of metals.[24] Other laser and experimental parameters such as the target–substrate distance,[18] the incident angle of the laser beam,[19] and the laser wavelength[20] have been studied to optimize the deposition process of the PLD. The effects of the pulse repetition rate on the crystalline structures of the films have been studied through experiments[25] and theoretical simulations.[26] However, the relationship among the surface morphology, the droplets, and the pulse repetition rate is not clear in the previous work. There is a close connection between the pulse repetition rate and the laser energy. Predictably, the pulse repetition rate has a significant effect on the formation of the droplets.

Even though the process involved laser ablation with ultra-short laser pulses and the laser–target interaction is still a matter of discussion, and models are only available for simple systems, investigators believe that the direct ejection of particles and droplets from the target is the apparent difference between a femtosecond laser and a nanosecond pulse.[27] Compared to the pulse femtosecond laser, the ablated species formed by the nanosecond pulses interact with the laser pulse itself. A non-equilibrium ablation process induced by the femtosecond laser causes the direct ejection of particles and

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droplets. The number density of the droplets strongly depends on the laser pulse duration. The published results show that the deposition processes with nanosecond pulse duration are more effective than those obtained with femtosecond laser pulses. Moreover, the surfaces of the deposited films under the nanosecond laser pulses are less covered by the droplets.[28] In order to evaluate the limits of the PLD technique and reduce the droplets, we investigate the Zr deposition process by using ultraviolet 248 nm laser pulses with a pulse duration of 25 ns.

To the best of our knowledge, little work has been reported on the Zr thin films deposited by PLD. In this study, we explore the effects of the pulse repetition rate on the surface morphology of the as-deposited Zr thin films. The study is aimed to reduce the dimension and the density of the droplets in such a process. This study lays a fundamental foundation for obtaining a better preparation condition for Zr films.

2. Model and method

Zr thin films approximately 60 nm to 320 nm in thickness were obtained by PLD onto Si (100) substrates. The KrF excimer laser with a wavelength of 248 nm was introduced into the chamber through a quartz window and impinged on the target surface with an angle of incidence of 45°. The purity of the Zr target was 99.99 % and the target was rotated to reduce drilling. To obtain uniform films, the substrate holder was rotated during the deposition process. The target and the substrate holder were rotated at the same rotating speed, which was about 12 revolutions per min. The laser spot size was about 1.5 mm^2, so the laser fluence was about 6.5 J/cm^2 . In order to remove the surface contaminations, the Zr target was cleaned by 3000 laser shots before depositions. The deposition time for all experiments was fixed at 120 min. The laser parameters and the experimental conditions are summarized in Table 1.

Table 1. Laser parameters and experimental conditions for Zr thin film deposition by PLD.

Laser parameter		Experimental condition	
Laser type	KrF, 248 nm	Vacuum level	1×10^{-5} Pa
Laser repetition rate	2–20 Hz	Substrate	Si (100)
Average laser fluence	6.5 J/cm^2	Target–substrate distance	50 mm
Pulse duration	25 ns	Substrate temperature	200 °C

The average deposition rate was taken through weighing each Si substrate before and after the deposition process. Grazing-incidence X-ray diffraction patterns of the films were obtained at room temperature using a Panalytical XRD X' pert PRO MPD diffractometer (Cu $K\alpha$ radiation) with a step of 0.03 and a count time of 2 s per step. The surface morphologies of the samples were characterized by means of scanning electron microscopy (SEM, Apollo 300 electron microscope of the CamScan Company) analysis. The root mean square (RMS) roughnesses and the average nanoparticle sizes of the films were measured by atomic force microscopy (AFM, SPA300HV).

3. Results and discussion

Figure 1(a) shows the grazing-incidence X-ray diffraction patterns of Zr films grown on Si (100) with various pulse repetition rates. The deposited Zr films exhibit a polycrystalline structure. The diffraction peaks in Fig. 1(a) show the α phase. Compared with the standard bulk Zr (JCPDS pattern #05-0665), an apparent preferential orientation in the (110) direction is observed for all films. The reflections at all angles show some broadening. Broadening in the XRD patterns can be attributed to smaller crystalline size and microstrain in the films. No other phases, such as zirconium silicide, are detected in the XRD patterns. Therefore, no interdiffusion exists between the Zr film and the Si substrate at 200 °C.[10] In Fig. 1(a), the film deposited at 2 Hz reveals a typical amorphous-like structure due to the insufficient film thickness.[29] The better crystalline quality obtained for Zr films grown at other pulse repetition rates can be ascribed to the increased thickness compared to the 2 Hz one. In fact, the higher deposition rate caused by a high pulse repetition rate makes the film exhibit a smooth morphology and a compact structure.[30] The data in Fig. 1(a) are completely consistent with the results shown in Fig. 4.

The average deposition rate decreases with increasing pulse repetition rate (Fig. 1(b)). A maximum error calculated as half the difference between the maximum and the minimum is taken into account for the deposition rate. The deposition rate significantly decreases from 0.0431 Å/pulse at 2 Hz to 0.0189 Å/pulse at 20 Hz. At a high pulse repetition rate, the pulse becomes unstable. A typical phenomenon is the pulse dropout. During a typical PLD process, the roughening of the target can cause a decrease in the deposition rate. The surface roughening of the target is an intrinsic shortcoming and cannot be eliminated completely. In fact, a higher pulse repetition rate can support a stronger interaction between the target and the incident laser pulse.[31] The amount of energy introduced to the target increases with increasing pulse repetition rate, which makes the target surface rougher. However, the energy introduced to the surface of the target per unit area and per unit time decreases because of the target roughening and the plume deflection effect,[32] resulting in the decrease of the average deposition rate. The changes of target morphology and the plume deflection effect have a decisive role on the decrease of the deposition rate.[32–34]

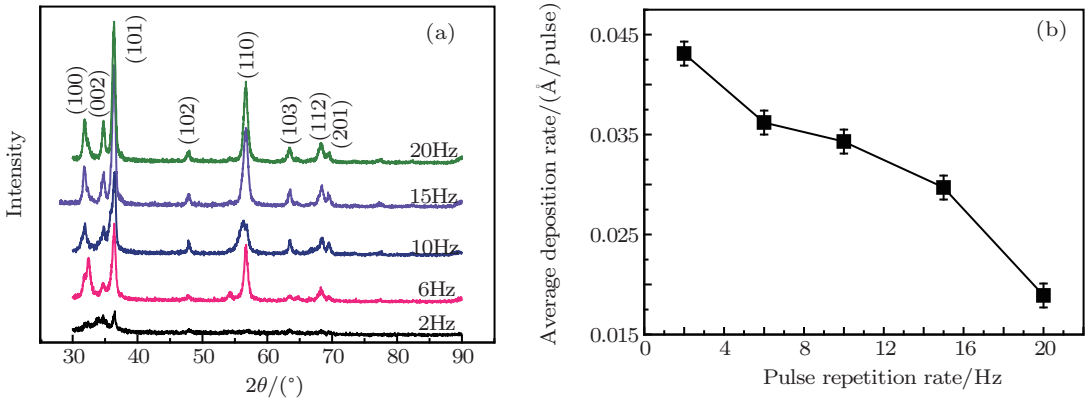


Fig. 1. (color online) (a) XRD patterns of Zr films with various pulse repetition rates, and (b) average deposition rate as a function of the pulse repetition rate (the solid line is a guide to the eye).

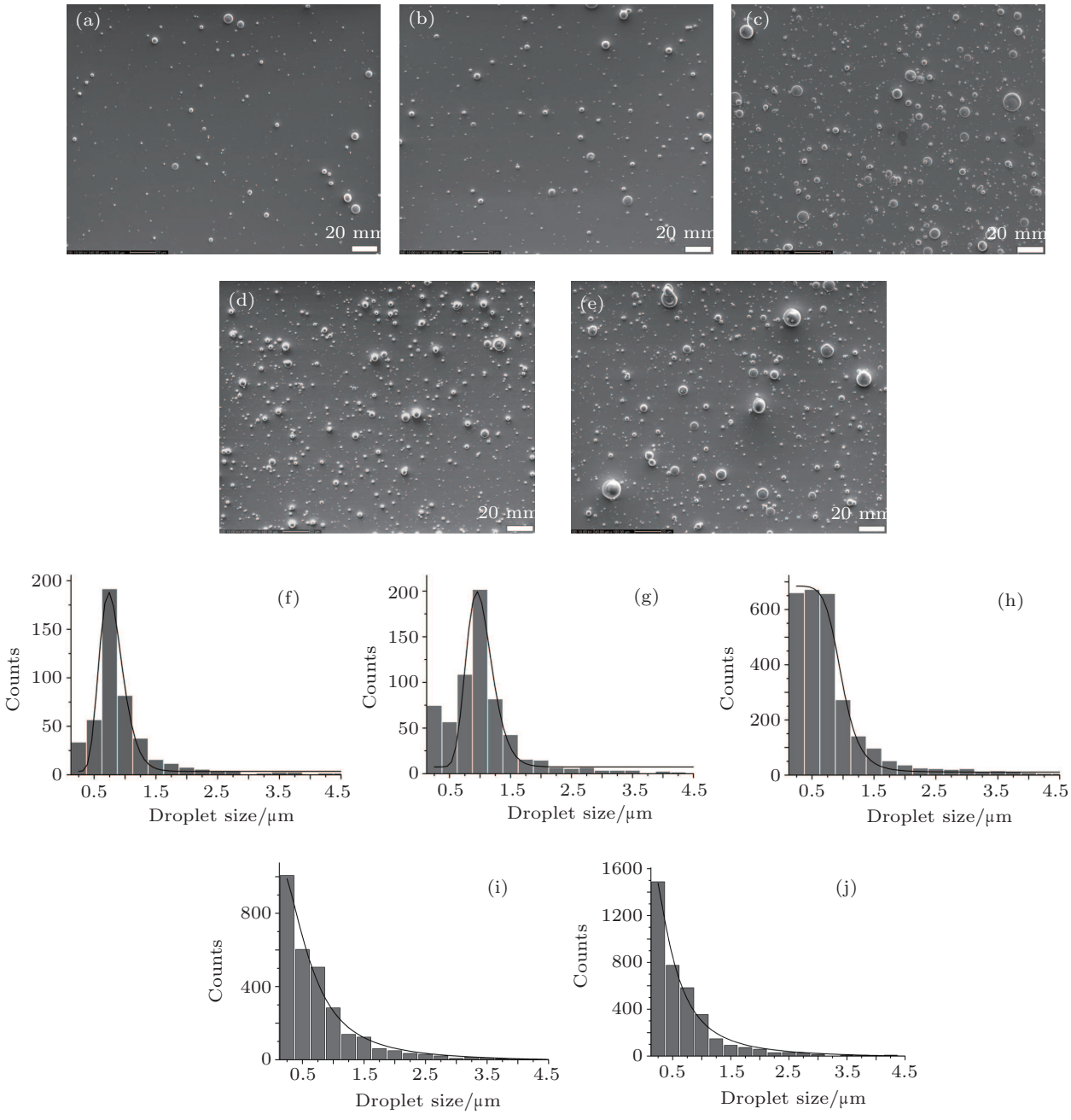


Fig. 2. (a)–(e) SEM images and (f)–(j) histograms of droplet size distribution of Zr films with various pulse repetition rates: (a) and (f) 2 Hz, (b) and (g) 6 Hz, (c) and (h) 10 Hz, (d) and (i) 15 Hz, (e) and (j) 20 Hz.

The surface morphologies of Zr films with various pulse repetition rates are depicted in Figs. 2(a)–2(e). All surfaces are sparsely covered by droplets, and most of the droplets on the Zr films vary in size from 0.01 μm to 10 μm. The droplets are composed of high-purity Zr, as detected by energy-dispersive X-ray spectroscopy. The histograms in Figs. 2(f)–2(j) corresponding to the SEM images clearly demonstrate the changes in the surface morphology.

A simple code in Matlab is used for the statistical analysis of the droplets. The SEM images and the statistical results show that the dimension and the density of the droplets increase with increasing pulse repetition rate. Data fitting to the statistical results show that figures 2(f) and 2(g) can be described as log-normal distributions represented by the equation

$$y = y_0 + \frac{A}{\sqrt{2\pi W x \exp\left(\dfrac{-\ln(x/x_0)^2}{2W^2}\right)}}. \quad (1)$$

The data shown in Figs. 2(h)–2(j) are in accordance with a logistic growth represented by the equation

$$y = A_2 + \frac{A_1 - A_2}{1 + (x/x_0)^p}, \quad (2)$$

where y is the count of the droplets on the surface of the as-deposited sample, x is the dimension of the droplets, and other quantities A, y_0, x_c, W, A_1, A_2, x_0, and p are all constants. Carrying on the data fitting to the size and the distribution of the droplets, we can predict the variation trend of the droplets. The presence of droplets on the surface of the as-deposited film is due to target ablation and plasma plume expansion during deposition. No simple technique can completely eliminate the droplets.[24]

One possible mechanism that can explain the formation of droplets with large dimension is the presence of a liquid layer under the Zr target surface. Under the high pulse repetition rate ablation, more and larger droplets are sprayed out from the ablation area.[23] During the initial stage of the laser ablation process, the liquid layer is very thin and can produce some droplets with smaller dimension. In Figs. 2(a) and 2(f), we find smaller and less droplets because of the thin liquid layer at a low pulse repetition rate. The amount of energy introduced to the target increases with increasing pulse repetition rate. When the laser energy continues to increase, the interaction between the laser and the target becomes stronger. Because the liquid becomes thicker due to more laser energy introduced at a higher pulse repetition rate, more and larger droplets are sprayed out from the liquid phase. The internal superheating of the liquid phase could be responsible for the expulsion of droplets under the interaction between the target and the laser shots.[35] The results are clearly shown in Fig. 2(a)–2(j).

The surface morphology of the Zr target after being irradiated with 32000 laser shots is shown in Fig. 3, where the red ellipses and circles are used to guide the eye. In the interior of the ellipses and the circles, we can clearly see the presence of droplets. The surface of the target is sparsely covered with a large number of droplets. The morphology, composition, and size of the droplets are similar than those on the surface of the Zr film. These droplets are sprayed out from the ablation area and have no chance to inject to the substrate surface. So, the droplets stay on the surface of the irradiated target. With the increase of time, the incident laser pulses cause the surface of the target to become rougher. The so-called ripple structure of the target induced by the laser shots has a great influence on the ejection of the droplets. This phenomenon also makes a great contribution to the number and the size variation of the droplets. The target with a much smoother morphology has more resistance to the spray of the droplets.[28] The experiment results shown in Fig. 2 are obtained at the same target. From 2 Hz to 20 Hz, the experiments are carried out according to the time order. With increasing pulse repetition rate, the target becomes progressively rougher, which makes the expulsion of the droplets more drastic. This is another explanation for the droplets size variation and the quantity change. In summary, the laser–target interaction plays a key role on the variation of the ejected droplets. From Fig. 3, we find that the source of the droplet is the liquid layer fomed under the target surface. The results in Figs. 2 and 3 are in accordance with the mechanism described above.

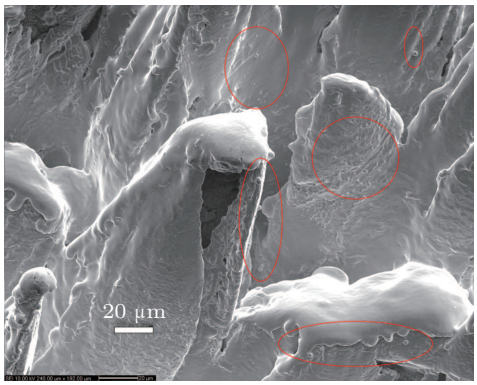


Fig. 3. (color online) SEM micrograph of Zr target after being irradiated with 32000 laser shots.

Figures 4(a)–4(e) show the AFM images of the Zr samples deposited at different pulse repetition rates. Roughness and topography are investigated using AFM. Figures 4(a)–4(e) show the morphologies of the as-deposited Zr films. It can be observed that the films deposited at different pulse repetition rates consist of densely packed nanoparticles. At a low pulse repetition rate, the pattern in Fig. 4(a) reveals an amorphous-like film surface. With increasing the pulse repetition rate, the film gradually shows a polycrystalline structure, as shown in Figs. 4(b)–4(e). The high energy introduced by a higher pulse repetition rate makes the film have a more compact structure.

The high instantaneous deposition rate due to the higher pulse repetition rate slows down the migration rate of atoms attached to the substrate and promotes the formation of a compact surface film.[30]

The RMS roughness is shown in Fig. 4(f). The roughness initially increases and then decreases with increasing pulse repetition rate. The pulse repetition rate significantly affects the surface morphology. The RMS roughness of the Zr film deposited at 10 Hz is 2.156 nm, reaching the maximum value. This irregular change may be influenced by the droplets and the valleys on the surface of the film. Moreover, the RMS roughness of the Zr film shows an irregular change, which is consistent with the result of a theoretical simulation.[25] A higher pulse repetition rate can lead to more and smaller islands. The small islands enhance the diffusion of atoms from the top of the growing island to a lower position on the substrate, resulting in a smoother film surface. Conversely, a lower pulse repetition rate can lead to lower island density, increased average island size, and diminished surface RMS roughness.[25] In general, the RMS roughness is low (< 2.2 nm), which makes the surface of the Zr film have a mirror-like appearance.

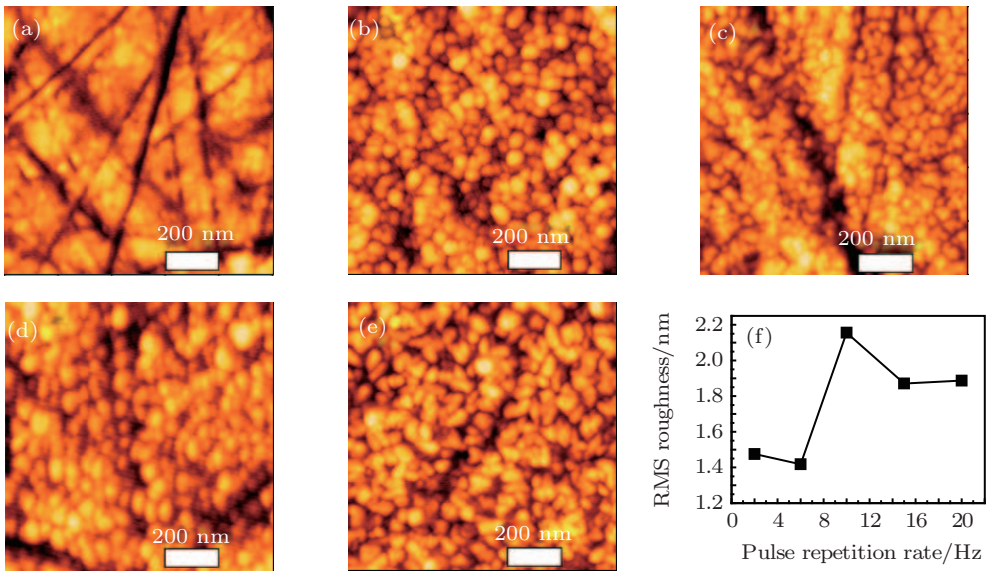


Fig. 4. (color online) (a)–(e) AFM images of as-deposited Zr films ((a) 2 Hz, (b) 6 Hz, (c) 10 Hz, (d) 15 Hz, (e) 20 Hz), and (f) the RMS roughness as a function of the pulse repetition rate.

4. Conclusion

Zr thin films grown on Si (100) by PLD at different pulse repetition rates are characterized. The XRD patterns of the Zr films exhibit a polycrystalline structure. No interdiffusion exists between the Zr film and the Si substrate at 200 °C. SEM patterns and statistical results reveal that the dimension and the density of the droplets increase with increasing pulse repetition rate. The deposition rate decreases with increasing pulse repetition rate because of the plume deflection effect and the target morphology variation. The AFM images indicate that a high pulse repetition rate can make the film have a compact and polycrystalline structure. A smoother film surface can be obtained by changing the pulse repetition rate during the deposition process. From the results, we find that a suitable pulse repetition rate should be selected for the deposition of Zr films.

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