DISTRIBUTION OF DROPLETS ON RUTHENIUM THIN FILMS PREPARED BY PULSE ND:YAG LASER

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Key words: Droplet, Pulsed laser deposition, Ruthenium

Abstract: Ruthenium (Ru) has been suggested as a potential material used for various applications in microelectronic industry. Pulsed laser deposition (PLD) enables the growth of Ru thin films at low temperatures. In this report, a thin layer of Ru has been grown on silicon (Si) substrates by pulsed laser deposition technique. When using the PLD technique, the grown layers very often exhibit some micrometer sized droplets. Although the droplets on the surface of the deposited Ru film can be dramatically reduced, there is still much effort being aimed at completely eliminating their presence, which could clearly restrict its applications. In this study, we report on the droplet formation on the deposited Ru thin films. The deposition processes were carried out at room temperature in vacuum environment with a pulsed laser Nd:YAG laser of 355 nm laser wavelength, employing various laser fluences ranging from 2 J/cm^2 to 8 J/cm^2. Therefore in this paper, we studied the droplets formation under the influence of pulsed laser deposition parameters on the ruthenium. The effect of the laser fluence on the droplets formation on the deposited Ru films was observed by field effect scanning electron microscopy (FESEM).

Porazdelitev kapljic na tankem filmu rutenija pripravljenega s pulznim laserjem Nd:YAG

Kjučne besede: kapljica, nanašanje s pulznim laserjem, rutenij

Izvleček: Rutenijum je bil predlagan kot možen material za različne uporabe v mikroelektronski industriji. Pulzno lasersko nanašanje (PLD) omogoča rast tankih filmov iz rutenija pri nizkih temperaturah. V prispevku popisujemo rast tanke plasti rutenija na silicijevem substratu s pomočjo tehnike PLD. Pri uporabi te tehnike se na rastočih plasteh razvijejo mikrometrske kapljice. Čeprav njihovo število lahko zmanjšamo, je bilo veliko truda vloženega, da bi njihov nastanek popolnoma onemogočili. V tem prispevku poročamo o tvorbi kapljic na rutenijevih tankih filmih. Nanašanje je potekalo pri sobni temperaturi v vakuumu s pomočjo pulznega laserja Nd:YAG pri valovni dolžini 355nm in pri različnih energijah, med 2 J/cm^2 in 8 J/cm^2. V prispevku torej obravnavamo nastanek kapljic pri različnih pogojih nanašanja rutenija. Vpliv parametrov nanašanja smo opazovali s pomočjo elektronske mikroskopije (FESEM).

1. Introduction

Pulsed laser deposition (PLD) has been a popular thin film deposition technique to grow a large variety of thin film materials covering inorganic, organic and high melting metal from solid targets /1,2/. This method is known to have the following advantages: (a) stoichiometric agreement with the target material /3/, (b) crystallinity enhancement due to the highly energetic species /4/ and (c) clean deposition due to particle ejection only by laser irradiation /5/. In view of these advantages, the development of new materials using PLD has advanced rapidly in comparison to other thin film deposition techniques. However, the formation of droplets using PLD which is detrimental to the quality of the thin film, is a major concern that needs to be properly addressed and studied /6/. These undesirable droplets deposition is main drawback for electronic device quality semiconductor films and optical films where droplets can introduce the formation of defects and scattering centers that lower the charge carrier mobility, shorten the carrier lifetime, and downgrade the damage threshold of optical films. To date, several methods /7/ have been attempted to eliminate the undesirable droplets,. However, it has been extremely challenging to eliminate the droplets without comprising the advantages of PLD. The droplets do not grow from the precipitation on film as a grain of irregular growth, but are ejected from the surface of the target.

In this paper, we investigate and study the formation of droplets on ruthenium (Ru) thin films grown by PLD, and its dependence on the laser fluence. For these experiments, Ru was used as the material for deposition due to its increasing popularity and widely acceptance in various applications in the microelectronic industry /8-12/. In order to obtain the relevant droplet distribution information, field effect scanning electron microscopy (FESEM) was employed to study the droplet formation on the surface of the Ru target and the deposited Ru thin films.

2. Experimental

The schematic diagram of the film preparation chamber is shown in Fig.1. Ruthenium thin films were deposited on silicon (Si) substrates at room temperature by pulsed laser deposition using a circular 2-inch diameter Ru target of 99.95 % purity. The substrates were set parallel to the target at a distance of 50 mm from the target. The pulsed laser beam with energy ranging from 17 mJ to 64 mJ was

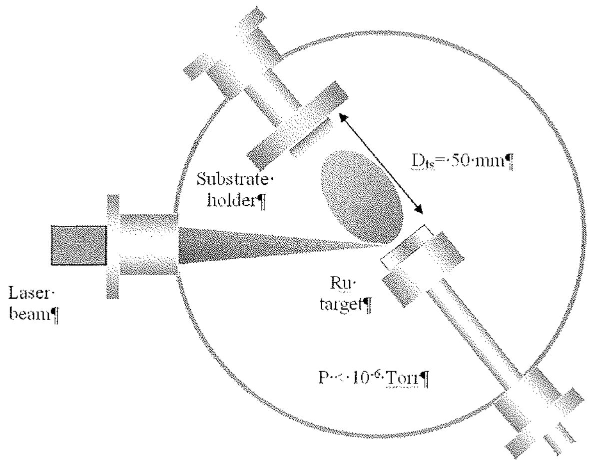

Fig. 1 Schematic diagram of the pulsed laser film deposition chamber

focused with a spherical lens onto a target with an area of 0.8 mm^2. The laser fluence was ranged from 2 J/cm^2 to 8 J/cm^2 with a repetition rate of 10 Hz. The laser beam struck on the target at an angle of 45° to the normal. The base pressure was lower than 2×10^{-6} Torr, achieved with a rotary pump coupled with a diffusion pump. The pulsed laser deposition processes were carried out in high vacuum environment with a pulsed Nd:YAG 355-nm laser source. The film deposition was run for a total number of irradiated laser pulses of 36,000.

The thickness of the pulsed laser deposited Ru films was characterized by Mahr surface profilometer after the deposition processes by measuring the step height between masked and unmasked regions on the substrate. The droplet formation on the surface of the Ru target and the deposited Ru thin films were observed by means of field emission scanning electron microscopy (FESEM) (LEO Electron Microscopy, LEO 1560). Detailed deposition conditions of the Ru films presented in this work are summarized in Table 1.

Table 1 Parameters for the pulsed laser deposited Ru

Laser	Nd:YAG laser (wavelength 355 nm)
Laser fluence	2 to 8 J/cm^2
Laser repetition rate	10 Hz
Targets	Ruthenium (purity: 99.95 %)
Substrates	(100) Si
Deposition time	60 min
Target-substrate distance	50 mm
Base pressure	$< 2 \times 10^{-6}$ Torr

3. Result and Discussion

Fig.2a shows the surface morphology of the Ru target before irradiation. After a few minutes of ablation which amounts to more than a few hundred laser pulses, high surface roughness of Ru target with ripple-mark was observed as shown in Fig. 2b. During PLD deposition, laser beam was directed onto the target, as the target was ablated until a certain depth in which the laser energy was rose above the threshold value where the surface evaporation happened and the molten pool was formed. The melting period was very short, and the melting zone was in minutes; as a result, the molten pool was compressed from inside of the target, and hence the formation of ripples. The ripples seem to organize and follow a certain growth direction with a small tilting angle from the surface.

The seemingly organized and same growth direction of the ripples might well attribute to the incident laser beam that was angled at 45° to the normal of the target during the deposition. As laser irradiation continues, droplets will form subsequently from the top of the ripples in the molten pool as shown in Fig 2c. The number of droplets continues to

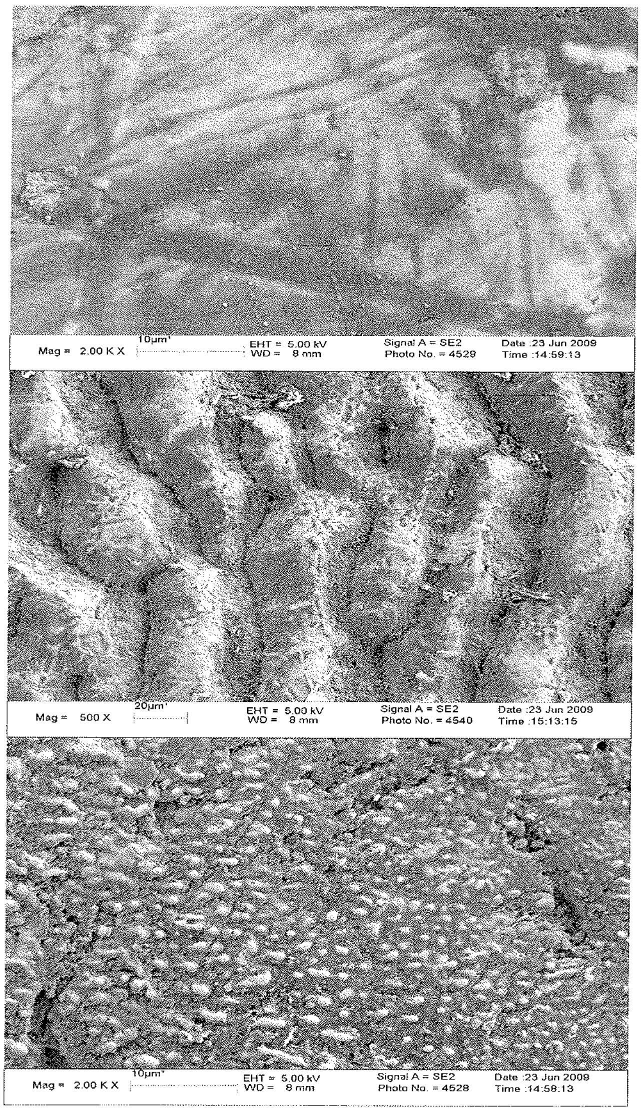

Fig. 2 The morphology of target surface before (upper), after few tens pulses (middle), and after 36,000 pulses (lower) of laser ablation.

increases as a result of continuous laser irradiation which lead to rougher surface morphology of the target and deepened laser /13/.

The thickness of Ru films deposited with laser fluence of 2 J/cm^2, 4 J/cm^2, 6 J/cm^2 and 8 J/cm^2 for duration of an hour were about 60 nm, 85 nm, 140 nm, and 180 nm as shown in Fig. 3 a, b, c, d, respectively. On the deposited Ru film surface, droplets are found as shown in Fig. 3. The presence of droplets which are rather spherical in shape on the surface of the PLD deposited Ru surface (Fig. 3) suggests that they are resulted from target splashing during laser target interaction and indicated that these droplets were (at least partially) molten before hitting the substrate. These observation of ripples on ablated target surface were also reported to contribute to the droplet formation /14/, which were formed as a result of Kevin-Helmholtz /15/ instability occurring in the interface between the molten layer and the plume. From Fig. 3, we can observe that the number of droplets and its size increase with increasing laser fluence. In order to quantitatively study the droplet formation, droplets with different sizes and diameters on FESEM images of 350 μm × 225 μm at the centre of the film were counted.

In our research, it is still not clearly understood for the mechanisms of the droplets formation. It is perhaps due to two mechanisms. First, it is due to the mechanically dislodged from the target due to laser-induced thermal and mechanical shock. Second, it is due to the rapid expansion of trapped gas bubbles beneath the surface during laser irradiation, causing forcible ejection of surface matter.

In our experiment, different droplet sizes ranging from 1 μm to 10 μm were observed as shown in Fig. 3. The number of droplets increased, and larger droplets were found with increasing laser fluence. The number of droplets and its diameter for different laser fluences are summarized in Fig. 4. From Fig. 4, it is worth noting that the droplets size falls mainly in the range between 2 to 6 μm. For Ru ablation with laser fluence of 4 to 8 J/cm^2, the size distribution of droplets follow a normal distribution curve with a peak number of droplets of 13, 38, and 65 respectively. Those droplets size which falls at the two ends of the normal distribution, increased the laser fluence seems to have less significant effect on increment of droplets count. In general, there exists threshold laser fluence, below which the droplets are negligible in size and number. Above the threshold laser fluence, the droplets number density increases rapidly with increasing laser fluence as shown in Fig 4b, c, and d. Through this experiment, we come to a simple approach to reduce the number of droplets by reducing the laser fluence to below the threshold level that causes the splashing of the molten layer. Under the Ru thin film deposition conditions in our study, we observed that the threshold laser fluence to be about 4 J/cm^2. Fig. 4 also shows that the total number of droplet increases rapidly from 22 to 73 and 147 with increasing

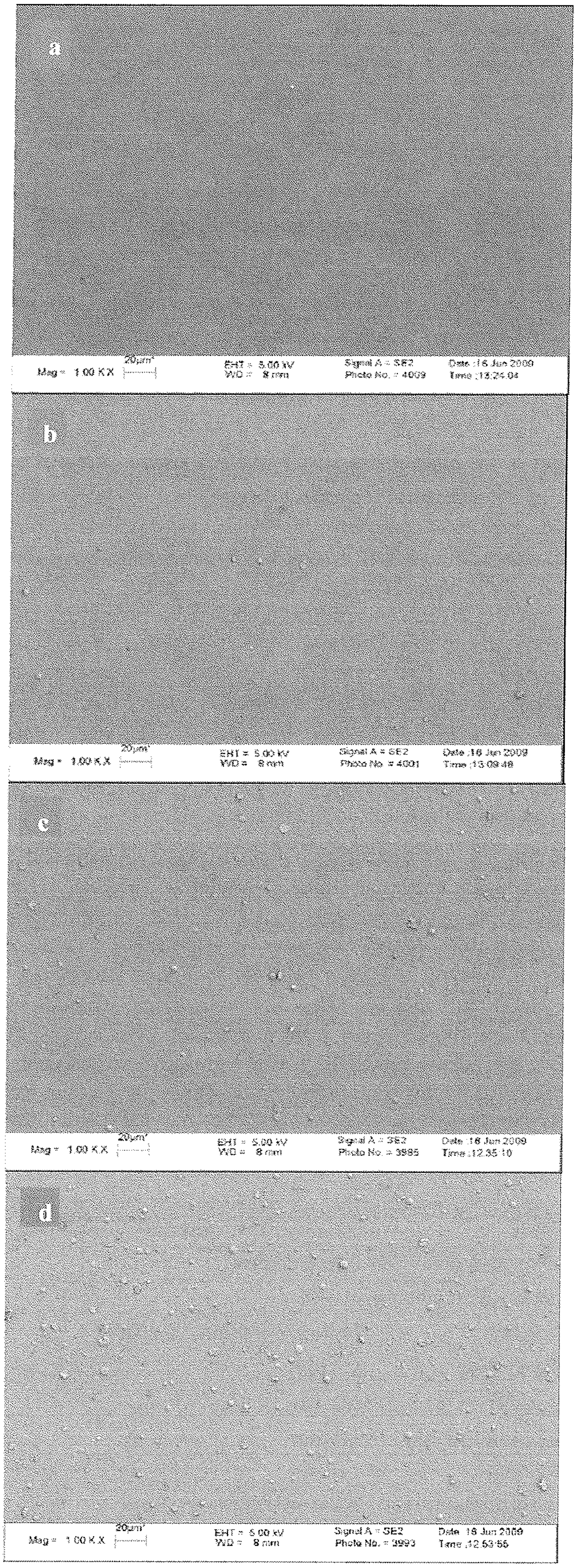

Fig. 3 The morphology of the deposited Ru film surface at laser fluence (a) 2 J/cm^2, (b) 4 J/cm^2, (c) 6 J/cm^2, and (d) 8 J/cm^2.

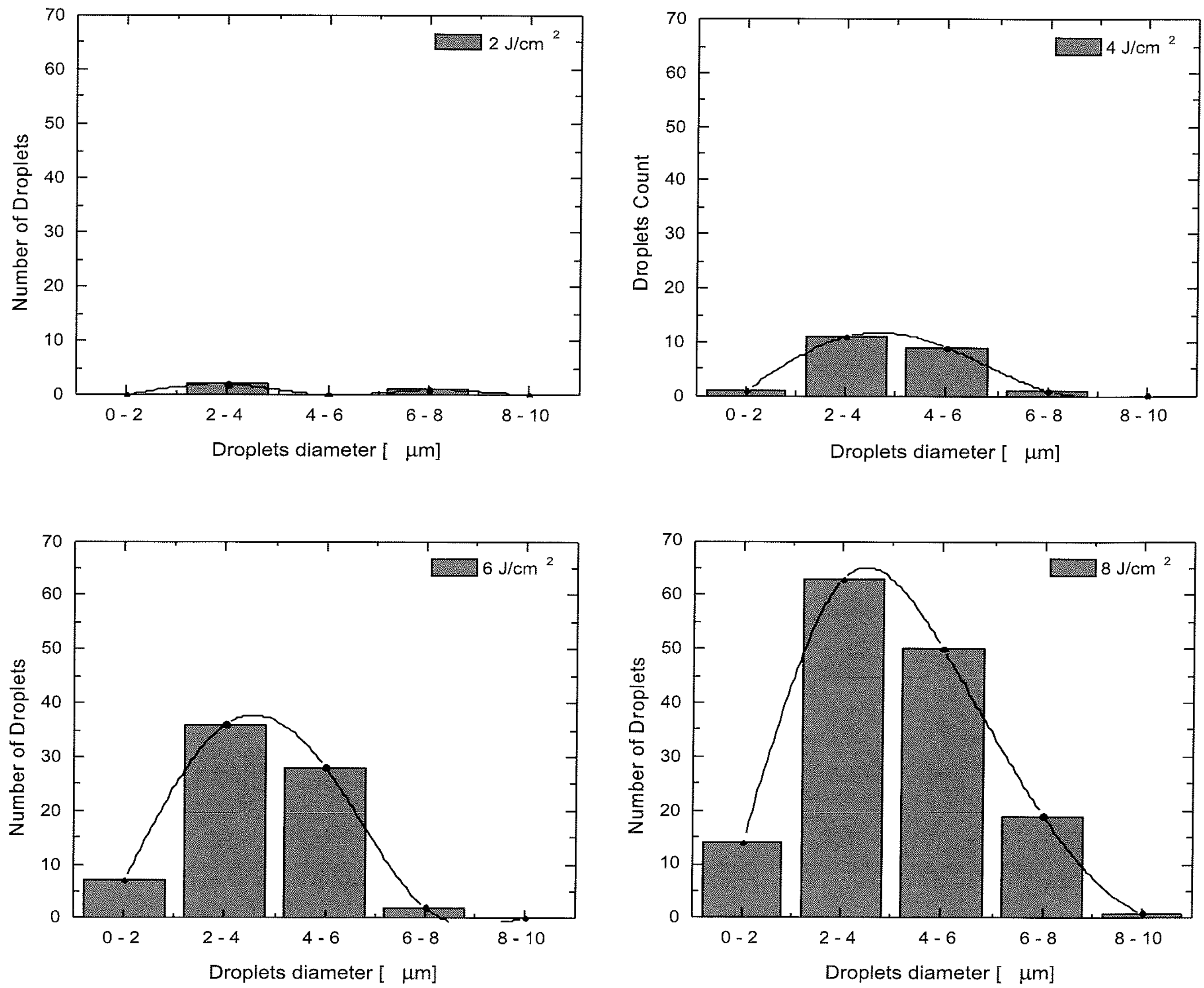

Fig. 4 Number of droplets for various droplet sizes at laser fluence (a) 2 J/cm^2, (b) 4 J/cm^2, (c) 6 J/cm^2, and (d) 8 J/cm^2.

fluence from 4 J/cm^2 to 6 J/cm^2 and 8 J/cm^2 respectively. This trend is in line with the observation made by van de Riet et al. /14/ and Dupendant et al. /16/ by comparing with different kinds of metals deposited using laser ablation.

The relationship of the number of droplets and laser fluence is shown in Fig. 5. It shows a general trend that the number of droplets increases with laser fluence. For droplets size of 2 to 4 μm and 4 to 6 μm, the increment of droplets is 61 and 50, respectively, when the laser fluence is increased from 2 to 8 J/cm^2. With compare to the droplets size of 0 to 2 μm and 6 to 8 μm, the droplets increasing is lesser with increment of 14 and 18, as the laser fluence increases from 2 to 8 J/cm^2. In addition, for droplets size of 8 to 10 μm, increasing the laser fluence from 2 to 8 J/cm^2, the droplets only increase by 1, therefore laser fluence seems to have less significant on the increment of the droplets in this region. This droplet distribution on deposition substrate can be described with a power-law for-

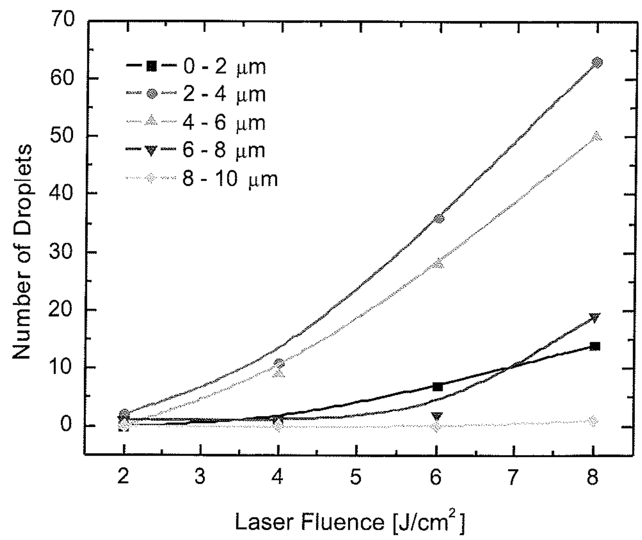

Fig. 5 Number of droplets as a function of laser fluence ranging from 2 J/cm^2 to 8 J/cm^2.

mula of the type $N(d) = a \times d^n$, where $N(d)$ is the density of droplets with diameter d (in μm) per square centimeter and laser pulse, a is a constant and n is the exponent of the power law /17/.

4. Conclusions

Droplets were formed from the top of the ripples that formed by the melt from laser beam on ruthenium target surface during the deposition. The initial morphology of the target was affected by the droplets formation on the target itself, which later are co-deposited to the surface of the growing substrate to form a thin Ru film with some micrometer size droplets on it. In this paper, droplets size between up to 10 μm was observed. The number of the droplets increases with increasing laser fluence. Droplets with size of 2 to 6 ěm were mainly seen on the deposited Ru films for all laser fluences. Therefore, it is observed that for Ru, as in our experiment, the threshold laser fluence is 4 J/cm^2 for 355 nm wavelength pulsed Nd:YAG laser. Below this threshold value, droplets formed on the deposited Ru films are less significant. Therefore, with the proper choice of laser fluence, droplets formation can be minimized.

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