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Study of the substructure in nanometer copper thin films treated by laser shock processing

Yinqun Hua (花银群)[1,2*], Qing Xue (薛　青)[2], Haixia Liu (刘海霞)[1], Yunxia Ye (叶云霞)[2], Ruifang Chen (陈瑞芳)[2], and Zeyan Ni (倪泽炎)[2]

[1]*School of Material Science and Engineering, Jiangsu University, Zhenjiang 212013, China*

[2]*School of Mechanical Engineering, Jiangsu University, Zhenjiang 212013, China*

**Corresponding author: huayq@ujs.edu.cn*

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We study nanometer copper thin films prepared by magnetron sputtering and treated with laser shock processing (LSP). We observe the formation of firstborn twin crystals and some complete twin crystals in the copper thin films. After LSP, scanning electron microscope (SEM) images show obvious plastic deformation of the copper grain on the film surface, dramatically increased grain size, and the appearance of a large number of twin crystals. Moreover, the width of the crystals is a few dozen nanometers, and the cross angle is more than or close to 90°. Many vacancy defects appear during the sliding of atomic plane, which leads to a faulty structure; however, no obvious dislocation is observed. These substructures play a significant role in improving the mechanical performance of nanometer copper thin films.

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Laser shock processing (LSP) is a new technology of surface improvement. In order to improve the mechanical performance of the materials, LSP uses metal with high power density (10^9 W/cm^2) and short pulse (ns level) laser irradiation. The latter rapidly vaporizes the material surface (or coating) and transforms it to plasma, allowing it to expand and explode. This process leads to the occurrence of a high pressure shock wave, which causes the plastic deformation on the surface. LSP technology has been widely used investigate intensifying non-ferrous and ferrous metal[1−6]. Lu *et al*. studied the plastic deformation of electrodeposition nanometer copper thin films[7−9]. In this letter, we study nanometer copper thin films on magnetron sputtering treated by LSP, as well as its substructure, with the aim of finding the application prospects of LSP in the field of nanometer thin films.

A copper target of 99.99% purity is used in this letter; it has a diameter of 60 mm and thickness of 3 mm. A Si substrate with a dimension of 1 × 1 (cm) was also used. The rinse process of the Si substrate followed. Here, we firstly put the substrate in a clean plastic cup and poured HF of 10% concentration to wash it for 1 min; then washed it with deionized water for 10 min; next, used an ultrasonic clearing machine to wash it again for 10 min while it was still in the deionized water, before finally drying it in the vacuum drying oven. During magnetron sputtering, the substrate temperature was set to 150 °C, and the working air pressure was at 0.5 Pa.

The experiment was conducted on neodymium glass high power laser, with wavelength of 1.06 μm, pulse width of 5 ns, spot diameter of 2 mm, and energy of 70 mJ. Figure 1 shows the configuration of the laser shock, in which the coating is self-made black paint with thickness of about 0.1 mm. We used this to coat the sample surface using a self-made liquid confinement material with good viscosity and good performance; the thickness was 0.8 mm.

Figure 2(a) shows the SEM image of the copper thin film. Prior to applying LSP, the film surface is quite smooth, compact, and with uniform grain size. Figure 2(b) shows the status after the LSP, we can see that grain size increased due to the effect of the laser wave that reduces surface roughness.

Figure 3 shows the transmission electron microscope (TEM) pictures of nanometer copper thin films. Figure 3(a) is shows the thin film on magnetron sputtering, with grain size that is less than 300 nm. The diffractive image in Fig. 3(b) indicates that the nanometer thin film is of non-crystal material without clear grain tropism. However, during the growth of the thin film, some first born twin crystals can be observed due to the effect of stress (Fig. 3(a)). At the same time, we also observe complete twin crystals in the film (Fig. 3(c)). However, we cannot find a large number of twin crystals. These are different from nanometer copper thin films made by electrical impulse deposition. Thus, the existence of stress is the essential condition of the growth of twinned crystal[7].

Due to the large difference of the physical mechanics between silicon and copper, when the film is cooled

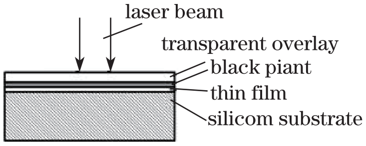

Fig. 1. Configuration of the laser shock.

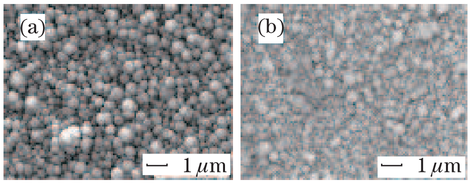

Fig. 2. Scanning electron microscope (SEM) images of copper thin film surface shapes (a) before and (b) after LSP.

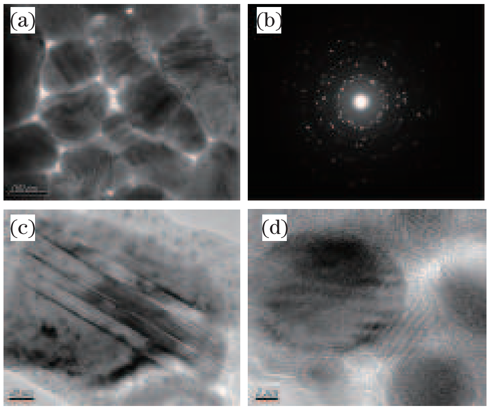

Fig. 3. Micro-optic structure of the copper thin film. (a) TEM image of the nanometer copper thin film; (b) diffractive image of the film; (c) complete twin crystals; (d) single crystal in copper thin film.

off after magnetron sputtering, the existence of stress becomes inevitable. This phenomenon leads to the formation of the twin crystals. Figure 3(d) shows the single crystal in copper thin film. When we observe the bottom right closely, it can be seen that the single crystal surface is consistent with the outside crystal lattice without a clear interface.

A large number of twin crystals are formed after performing LSP on the nanometer copper thin film, which is similar to the result reported by Shen *et al*[8,9]. In addition, we find a significant phenomenon, in which the grain size increases after LSP (Fig. 4(a)). Judging from the length of the twinned crystal in Fig. 4(b), the longest twinned crystal is about 1 μm. This phenomenon disputes the theory that laser shock results in refined and broken grains. After LSP, trace amounts of black paint remain on the sample surface, indicating that the crystal did not recrystallize. In the TEM observations, there are no signs or evidence of grain remelting; thus, the thermal effect of laser shock can be ruled out. We can see from Fig. 2(b) that the grain in the film underwent plastic deformation, and the size is increased. Thus, we believe that grain size increase is caused by the plastic deformation due to laser shock and not by thermal effect. The thin films are quite different from block materials. The grain orientation in the film is very weak, whereas the grain has clear orientation in the block material, as seen in the diffraction picture. Thus, it can be inferred that the grain in the film is not a conventionally crystallographic grain, and is more likely a kind of state grain. Furthermore, there are both crystalline and noncrystalline states in the film. As shown in Fig. 3(d), the grain size is very small, and the difference between the crystal and transition zone is not obvious, because the grain continues to grow under external force. Therefore, as the outcome of this experiment shows, under great stress, film grain does not refine or break but grows instead. Meanwhile, we do not find any growth in the block metal after LSP, which is one of the essential differences between film grain and block metal grain.

After LSP, there is a large number of twin crystals in the film. Such crystals have a variety of shapes, and some twin crystals have wide-angle connections with the others (Fig. 4(a)). There is also a step structure in the twin crystal, as can be seen from the longest twin crystal in Fig. 4(b), which is similar with the martensitic phase transformation step growth in block metal after LSP. Both phenomena are caused by the great stress and strain of laser shock. In addition, the angle of the step structure is about 120° (Fig. 4(c)), and some twin crystals have different strip widths and coherent interface between the twin crystals.

We observe residual stress in the film after the LSP, resulting in numerous small holes in the material, These so-called stress concentration holes intensify the material, thereby leading to space strengthening (Fig. 5 (a)).

Figure 5(b) shows the appearance of faults in the structure after LSP. A fault is a kind of plane defect, which also intensifies the material. This is quite different from the block metal after LSP (i.e., a great amount of fault would appear in normal block metal after LSP). In comparison, in our experiment no clear fault is found. First, it has something to do with the original structure of the film. During the growth of the film, there are few original line defects; if there are many original line defects, then these are enlarged under the effect of laser wave, causing more faults as seen from the TEM image. Second, because the copper thin film is of high purity, it is unlikely to have lattice distortion. Thus, it is easy to understand why there is no clear dislocation defect. The substructural change is characterized by sliding surface deformation. Dislocation glide is represented by line slip deformation, which requires less strain energy than sliding surface deformation. In fact, a great amount of fault can be found even in regular deformation. Meanwhile, sliding surface deformation requires more energy than dislocation glide. Laser shock wave provides necessary conditions for its phase transformation, including high pressure, high stress, and super plastic deformation. Thus, a large number of twin crystals, vacancy defects and some faults appear in the substructure, instead of faults.

In conclusion, there are some twin crystals in the original nanometer copper thin film. When there is remaining stress, twinned phase transformation takes place–some become twin crystals and some become firstborn twinned crystals. The grain of the nanometer thin film grows, especially in twin crystals. Once copper thin film is treated by laser, the substructure

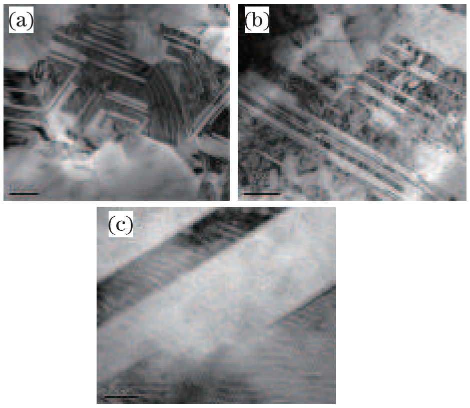

Fig. 4. Microstructure of the copper thin film induced by laser wave. (a) Grain size after the LSP, (b) the longest twinned crystal, and (c) the step structure.

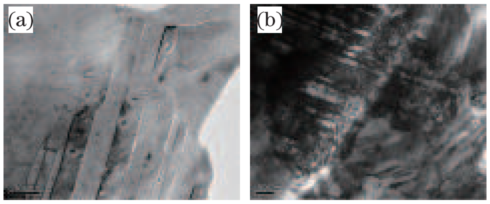

Fig. 5. Substructure defect. (a) Holes in the material after shock and (b) faults in the structure.

acquires a twinned crystal structure. Under the effect of high stress and high strain rate laser shock wave, superplastic deformation takes place in the film, causing the original firstborn twin crystals to change into twin crystals. This phenomenon also leads to the formation of a large number of new twin crystals with a variety of shapes. After treating thin film by laser, a large number of vacancy defects appear. Due to the fact that the substructure in the film is mainly deformed twinned crystal, the twinned crystal deformation is the slip plane. The slip plane is where the whole sliding of the atomic plane occurs. When some atoms cannot slide together with the plane, then some defects appear, thereby forming small holes where stress concentrates. Thus, these holes are caused by the effect of stress. Faults appear, along with slight dislocation, when the copper thin films are treated by LSP.

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