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# Surface morphology study on chromium oxide growth on Cr films by Nd-YAG laser oxidation process

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**Abstract**

Grain sized (60–100 nm) $Cr_2O_3$ thin films were prepared on Cr thin film surfaces by Nd-YAG laser photothermal oxidation process. Surface morphology study showed crack-free short plateau-like oxide films formed. Increase of dislocation density after pulsed laser irradiation was found. Thin film external surfaces, grain boundaries and dislocations are main paths of laser surface oxidation. Pinning and sealing of grain boundary was the reason that deeper oxidation did not produce. Grain growth and agglomeration of Cr sub-layer yielded tensile stress on the surface $Cr_2O_3$ thin film. It was the reason that short plateau-like surface morphology formed and cracks appeared sometimes. In oxygen annealing at 700 °C, grain boundaries were considered not to be pinned at the surface, mixture diffusion was main mechanism in growth of oxide. Compression stress development in whole film led to extrusion of grains that was the reason that multiple appearances such as pyramid-like and nutshell-like morphology formed.



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*Keywords:* Laser oxidation; Thin oxide film; Oxidation mechanism; Morphology

## 1. Introduction

For the last two decades of study and development, many oxide films have been found to serve various functions of their applications. For example, $Cu_2O$ thin films for photovoltaic device, ZnO for UV emission, $CeO_2$ for preventing heat-diffusion between Si and YBCO, and $TiO_2$ films have been expected to be high dielectric usage. They have been often fabricated by PLD and sol–gel [1–4]. Recently much attention is paid to fabricate novel oxide films from metal films by direct oxidation processes. $PdO_2$ from Pd metal film oxidation in $O_2$ is expected to be field emitter array for vacuum microelectronic devices [5], $Cr_2O_3$ film is expected to being a native oxide on Cr coated substrate as protective layer in non-photolithographic study [6]. It is certain that different surface morphology are formed for corresponding applications, $PdO_2$ film which is expected to being field emitter array forms hillock surface but protective $Cr_2O_3$ layer is expected to forming comparatively smooth and crack-free surface morphology.

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In our study, Nd-YAG laser was applied to rapid selective oxidation Cr films, crack-free $Cr_2O_3$ films on Cr films were obtained. Morphology study showed that it was strong different between laser rapid selective oxidation and annealing in oxygen. Different growth mechanisms that showed different evolution of surface morphology were suggested. They did not only relate to the surface stress regime but also to the oxidation mechanism and crystal structure. Their different mechanisms were discussed in this paper. Direct experimental data on materials were provided for non-photolithographic study. The suggestion about oxidation mechanism by pulsed laser was novel, it was a supplement to other studies that invented equipment and established heat-diffusion numerical model in this field [6,7].

## 2. Experimental

Polycrystalline Cr films with a thickness 2 μm were deposited on thermally grown $SiO_2$/Si(1 1 1) and glass substrates by thermal evaporation at 200 °C of substrates, and vacuum below $10^{-4}$ Pa. A Nd-YAG laser with 1062 nm wavelength was used. Samples were mounted on a computer-drivering X–Y stage to allow their displacement under the laser beam with pre-set scan velocity in order to increase of oxidation area. Typically, laser beam with a spot size of 1 mm diameter was under focused on the sample surface in oxygen, laser energy density was from 20 to 100 mJ/cm$^2$, this was lower than the ablation density. For comparison Cr film samples that were prepared on $SiO_2$/Si substrates were annealed in oxygen at 700 °C. The surface morphology and crystallographic structure were studied with scanning electron microscope (SEM) and X-ray diffractometer (XRD) (Cu Kα was used). Au layers with about 100 angstroms thickness were deposited on every sample by ion sputter for the sake of improvement of electric conductivity for SEM observation.

## 3. Results and discussion

Fig. 1 shows that laser parameter had strong influence on the surface morphology of samples, and it had a narrow laser energy density window zone for

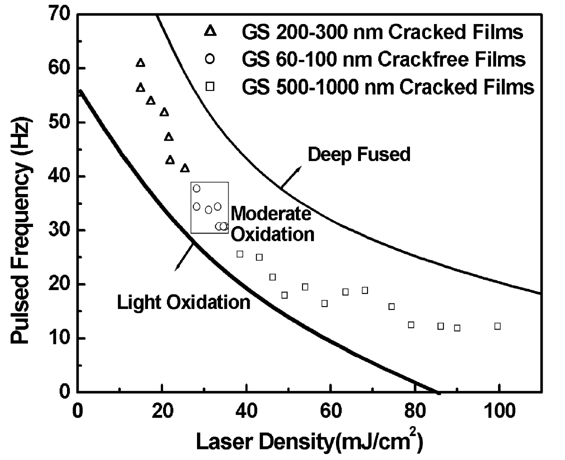


Fig. 1. Oxide surface grain size is dependent on laser density. Moderate laser density (25–35 mJ/cm$^2$) produce 60–100 nm grain sized crack-free oxide films (○); slightly larger power than moderate laser energy density (35–100 mJ/cm$^2$) produce 2–5 μm sized domains on surfaces (□); smaller laser density but overlapped laser spots (10–25 mJ/cm$^2$, 40–80 Hz) produce little larger grain sized (200–300 nm) cracked oxide films (△).

moderate oxidation rate. When larger laser energy density was employed, Cr films were fused deeply that all Cr films were oxidized. Film surfaces were poor. When smaller laser energy density was employed, Cr films were oxidized lightly or no oxide layers formed. Moderate oxide films were shown in Fig. 2. Sample surface with Cr film was oxidized and became

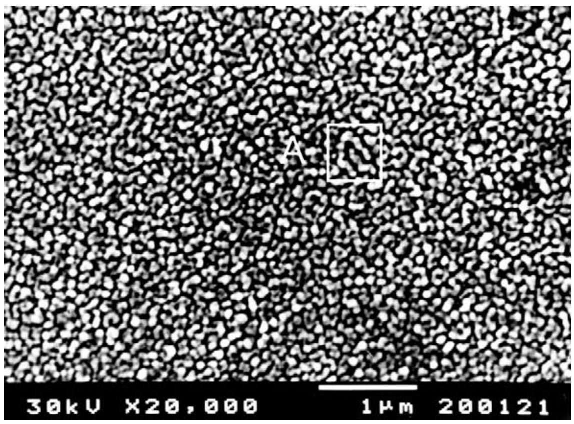


Fig. 2. Surface SEM image of nanocrystalline $Cr_2O_3$ films by pulsed laser oxidation, 60–100 nm grain sized and crack-free, laser density 30 mJ/cm$^2$, sintering was found among some grains in rectangle area that marked with A.

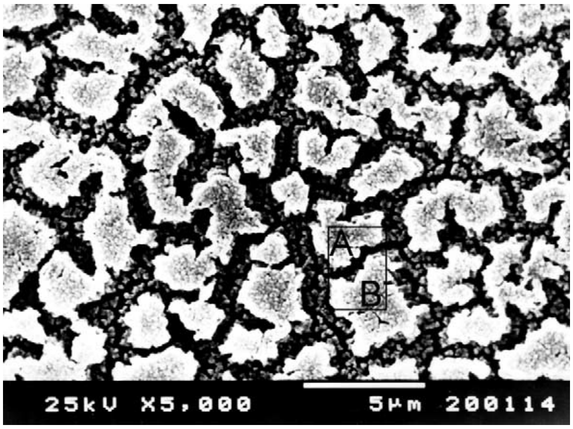

Fig. 3. SEM image of cracked micro-crystalline surface, two domains mark with A and B which consist of several 500–1000 nm agglomerated $Cr_2O_3$ grains, laser energy density 35–100 mJ/cm$^2$, cracks in domains (A and B) boundary.

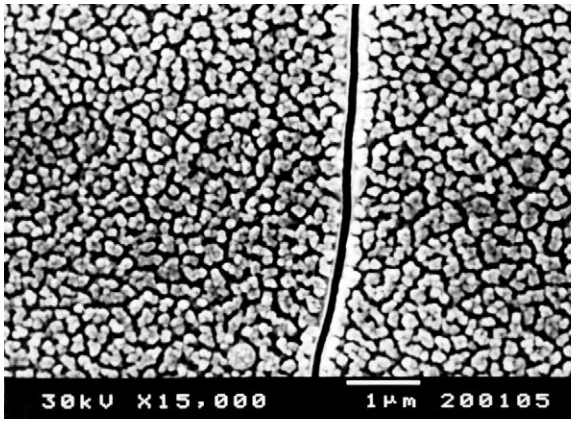

Fig. 4. SEM image of cracked submicro-crystalline surface films with grain size about 200–300 nm produced by overlapped laser spots (10–25 mJ/cm$^2$, 40–80 Hz).

polycrystalline surface with grain size (GS) about 60–100 nm. It was crack-free. Only a little grains sintering (mark A) was found. Fig. 3 shows that slightly larger power than moderate laser energy density produced larger oxidation rate that thicker Cr films were oxidized, 2–5 μm sized domains (mark A and B) in which several 500 nm smaller agglomerated grains produced. Allover cracks (between mark A and B) in domains boundaries formed. Fig. 4 shows that overlapped laser spots produced little larger grain sized (200–300 nm) cracked oxide films. In fact they were all $Cr_2O_3$ polycrystalline layers.

In short, all surface morphology is short plateau-like whether it is crack-free or cracked under our laser rapid oxidation condition. However, many other studies about thin metal films under annealing or oxygen annealing [5,8,9] show hillocks or wrinkling films form without crack, often stress by oxidation are thought that it is main reason for the above. All their results are reliable; another experiment [10] gives a proof. We agree this point completely. In our experimental conditions, we found difference morphology between rapid pulsed laser oxidized Cr films and oxygen annealing Cr films. We consider that short-circuit diffusion and sintering are important in oxidation mechanism under our experimental conditions. Shrinkage of Cr sub-layer of surface $Cr_2O_3$ film during laser irradiation produces tensile stress to the surface $Cr_2O_3$ film, so those short plateau forms.

As we all know that polycrystalline metal films contain dislocations, grain boundaries, and external surfaces. Diffusion along such line and surface defects is more rapid than the diffusion of atoms in grain lattice. Although direct quantitative measurements of diffusion along line and surface defects are experimentally more difficult to perform than those of lattice diffusion, available data show that diffusion coefficients for short-circuit diffusion are $10^4$–$10^6$ times larger than the lattice diffusion coefficient. And the activation energies for short-circuit diffusion are 0.5–0.7 times that for lattice diffusion. Dislocation diffusion has higher activation energy than for grain boundary diffusion. This makes short-circuit diffusion increasingly important the lower the temperature [11].

### *3.1. Laser oxidation*

#### *3.1.1. Oxidation along dislocation, external surface and grain boundary*

For laser rapid oxidation, pulsed laser duration was so short that photothermal oxidation produced during $10^{-3}$ s. Oxidation was only found within thin surface of Cr film. When the Cr film surfaces were irradiated, adsorption of oxygen started in external surfaces and boundaries of nanometer-sized Cr grains, they were oxidized and became $Cr_2O_3$. Before this step dislocation apply an important role like external surface and grain boundary, Fig. 5. XRD shows that GS of Cr film

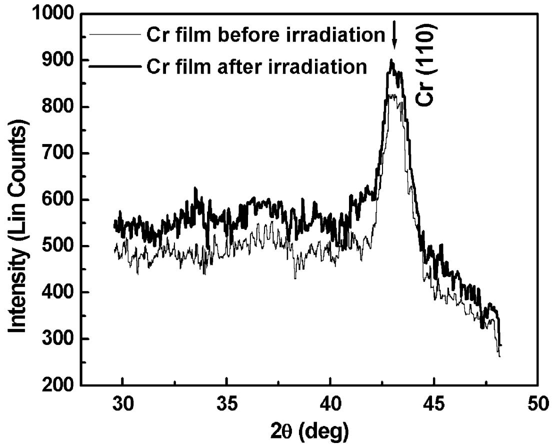


Fig. 5. XRD patterns of Cr films before (the below line) and after (the upper line) laser irradiation.

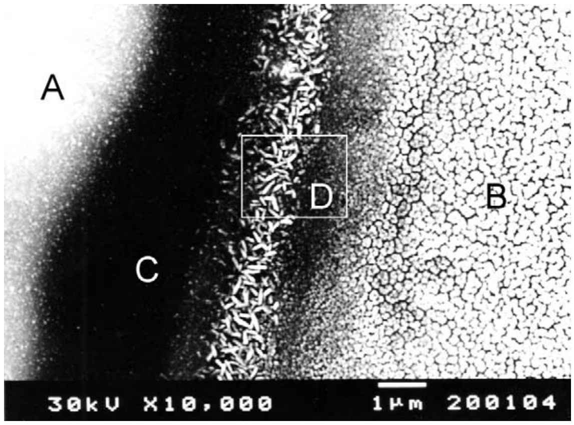


Fig. 6. SEM image of willow leaf-like $Cr_2O_3$ (marked by D) inside crack. Black zone C marks no oxidation spacing between two irradiation zones (A and B) by two continual laser spots.

is about 13.4 nm from computer-calculated value by integral width of diffraction line, and its dislocation density about 1.5E13 $cm^{-2}$, much higher than the coarse crystalline materials. Effect of dislocation is not to be ignored. Furthermore after irradiation by smaller energy density laser (5 $mJ/cm^2$, no sintering and oxidation) it adds up to 1.9E13 $cm^{-2}$ (no variation on GS). This phenomenon has been certain in our study by XRD in different location of laser scanning line. It showed that increase of dislocation density after pulsed laser irradiation is certain. The dislocation movement and generation are active before grain boundaries and external surfaces were oxidized. So, we suggested that besides surface oxidation and grain boundary oxidation, dislocation was the third path of oxidation, it led to oxidation from surface and grain boundary to the grain lattice inside before pinning and sealing the surface.

### 3.1.2. Sintering of $Cr_2O_3$ grains

During oxidation volume of Cr film will increase, Pilling–Bedworth ratio (PBR, the volume of oxide divided by that of the metal from which it is formed) [11] is 2.07 and is larger than 1. Every grain will grow; sintering of $Cr_2O_3$ grains (about 20 nm) produce and $Cr_2O_3$ grains agglomerate each other to form about 60–100 nm sized $Cr_2O_3$ grains. Large shrinkage will associate with the overall sintering process by viscous flow. If sintering shrinkage is equal to the $Cr_2O_3$ growth rate in plane direction, a completely dense films form, and no residual stress produce. But in fact sintering shrinkage do not exceed 100%, so surface $Cr_2O_3$ films will expand. Once a completely dense films form, deep oxidation will be inhibited because short-circuit diffusion paths vanish. Cr grain boundaries are pinned and could not migrate again. It is so clearly that Cr film surface oxidation has strong relation with the adsorption of oxygen and oxidation along grain boundary (see Fig. 6). There are many $Cr_2O_3$ scales, which look like willow leafs (D) at the edge of crack. The crack is in the spacing between two irradiation zones (A and B) by two continual laser spots. In this spacing, oxidation is weaker than the center of laser spot because that the laser spot is Gauss mode. It is indicated that when pinning grain boundary is cracked, grain boundary expose. Oxygen will be easily adsorbed and it will easy diffuse along grain boundaries. That is to say after dense $Cr_2O_3$ film formation, sealing of the grain boundary is unavoidable, deeper oxidation could not produce.

### 3.1.3. Cr sub-layer under surface $Cr_2O_3$ film

During laser oxidation of surface layer, thermal conduction on Cr sub-layer under surface $Cr_2O_3$ films produce. Nanometer-sized Cr grains will grow and agglomerate. If we express initial GS and that after irradiation by using their average grain radius $r_0$ and $r$, stress from film shrinkage by internal grain boundary decrease can be expressed by formula [12]:

$$\sigma = \frac{E}{2(1-\nu)}\delta\beta\left(\frac{1}{r_0}-\frac{1}{r}\right) \quad (1)$$

Here, $E/(1-\nu)$ is the biaxial elastic modulus expressed in terms of Young's modulus $E$, the Poisson's ratio $\nu$, $\delta$ the grain boundary thickness, and $\beta$ is the relative density difference between the lattice and the grain boundary. So surface $Cr_2O_3$ film will be tensile by sub-layer Cr film. The more growth of this Cr film by thermal effect the bigger stress $\sigma$ produces. If this stress is lower the tensile strength of surface $Cr_2O_3$ film, surface $Cr_2O_3$ film will be crack-free. However, when bigger laser power density or smaller laser power but overlapped laser spot was applied, this sub-layer will be thicker than that moderate laser power was done, bigger grain growth and agglomeration will produce bigger stress. If it exceeds the tensile strength of surface $Cr_2O_3$ film, $Cr_2O_3$ film will be cracked. Stress that yields in such film lead to film cracking in the case of tension.

### 3.2. *Comparison experiment: oxygen annealing of polycrystalline Cr film*

Comparison experiments were conducted to find different mechanism between laser oxidation and oxygen annealing. After 2 h oxygen annealing at 700 °C, $Cr_2O_3$ films were found that they have multiple surface morphology such as nutshell, pyramid with 60–120°, see Fig. 7. It is result that $Cr_2O_3$ with hexagonal structure ($\gamma = 120°$) will grow along certain crystallographic planes. If oxide is cubic structure, the hillock should form as $PdO_2$ in [5].

For the low temperature growth, growth is slowly and mixture diffusion (lattice diffusion and short-circuit diffusion) is main mechanism in growth. Diffusion coefficient is written [13]:

$$D = fD_{GB} + (1-f)D_L \quad (2)$$

Here, $D_L$ and $D_{GB}$ are diffusion coefficients for limiting atoms to diffuse through the lattice and along grain boundaries respectively, $f$ is the fraction of lattice sites which belong to the short-circuits. For oxygen annealing, near-atmospheric oxygen pressure, we do not consider nanometer-sized grains and their boundaries are pinned at the surface. The lattice diffusion becomes main motility for growth. So, all Cr film is oxide. Taking into account the grain boundary diffusion coefficients is larger than that in lattice, lattice diffusion is the limiting stage for growth. The diffusion coefficient of oxygen in $Cr_2O_3$ lattices is 100 times larger than Cr in it [10,14]. So, it is conclude that Cr diffusion is the limiting stage in $Cr_2O_3$ growth and $Cr_2O_3$ scales grow by counter-diffusion of Cr and O atoms along grain boundaries and Cr/$Cr_2O_3$ interface. As a result $Cr_2O_3$ scales grow along both perpendicular and parallel direction with the Cr surface. Large stresses from volume increase during Cr/$Cr_2O_3$ reaction can bring about scale extrusion from Cr surface because that the Cr film is fixed by $SiO_2$ substrate. Growth along parallel direction of substrate is inhabited. Compression stress that develops in such film can lead to nutshell-like, pyramid-like and hillock-like [15] surface. Relaxation itself produces at same time. Pinning will not form because lattice diffusion is adequate in slowly oxidation.

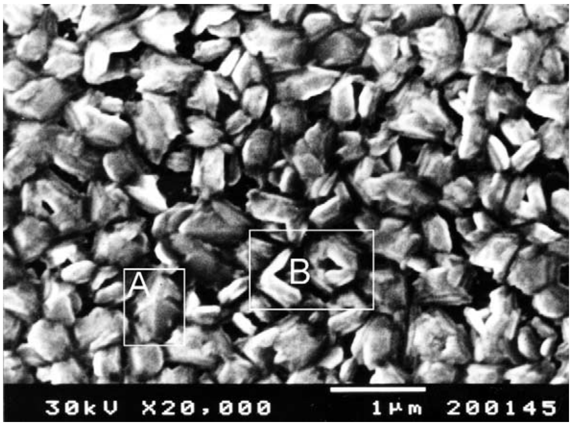


Fig. 7. SEM image of Cr film sample surface after oxygen annealing at 700 °C, pyramid-like (A) and nutshell-like (B) with 60 and 120° form.

## 4. Conclusion

Crack-free short plateaus-like $Cr_2O_3$ films with grain size about 60–100 nm are obtained by pulsed laser oxidation from Cr films. Surface and grain boundary oxidation pins the film. As deep oxidation, crack is found. External surface, grain boundary and dislocation are main paths of O atoms and Cr atoms diffusion in laser rapid oxidation. Sintering of $Cr_2O_3$ grains is found in $Cr_2O_3$ film growth by pulsed laser. Tensile stresses from sub-layer under surface $Cr_2O_3$ films lead to short plateau-like surface morphology, and likewise it is the reason of crack formation in

$Cr_2O_3$ film. There are three differences between laser oxidation and oxygen annealing of Cr films. Firstly, short-circuit diffusion that along external surface, grain boundary and dislocation paths is main oxidation mechanism in laser oxidation. Mixture diffusion includes both lattice and short-circuit diffusion is main mechanism in oxygen annealing. Secondly, grain boundary in laser oxidation is pinned and sealed, the later not. Thirdly, in laser oxidation surface oxide layer is subject to tensile stress but later to compression stress. These are root causes of different growth mechanism between laser oxidation and oxygen anneals which lead to different surface morphology.

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