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Oxidation behavior of Cr films by Nd:YAG pulsed laser

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Abstract

Surface oxidation of Cr films by laser was studied by scanning electron microscope and X-ray diffraction. Oxide growth is homogeneous with long pulse laser (100 μs pulse duration) but it has preferred orientation along (1 1 6) with short pulse laser irradiation (100 ns pulse duration). Lattice contraction results from internal growth stresses.
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1. Introduction

Oxide films synthesized by non-vacuum methods have been rapidly improved recently. Ordering PdO_2 film was synthesized from polycrystalline Pd film by annealing in oxygen [1]. TiO_2 film was produced from Ti films through local anodic oxidation by using an atomic force microscope [2]. TiO_2 film was made on Ti substrates by microarc oxidation [3]. Pulsed laser irradiation photochemical processing was employed to oxidize the surface of metal or metal films in order to synthesize oxide films. It is possible to use this method in functional film synthesis and maskless non-photolithography process. Previous reports about metal film oxidation by pulsed laser were concerned with the writing resolution of the laser beam and its thermal field [4–6], which are all important in laser oxidation. However, microstructure and oxidation behaviors were seldom studied. In our study, scanning electron microscope (SEM) and X-ray diffraction (XRD) were applied to investigate the microstructure of laser oxidized Cr films. It was shown that oxidation behaviour of nanocrystalline Cr films is significantly influenced by pulsed laser parameters. Internal stresses played an important role in surface microstructure formation.

2. Experimental procedures

Polycrystalline Cr films with thickness 2 μm were deposited by thermal evaporating Cr onto glass substrates by Mo boat with vacuum below 10^{-4} Pa. The temperature of the glass substrates was controlled at 250 °C during Cr film deposition.

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Table 1
Typical laser irradiation parameters and types of corresponding oxide films

Sample	Pulse duration (μs)	Energy density (mJ/cm^2)	Characteristics of oxide films	Corresponding figures of surface morphology
1	0.1	100	No oxidizing, nanosized spots	Fig. 2
2	100	20	Oxide inherited Cr film texture	Fig. 3
3	1	30	Dense oxide film	Fig. 4
4	100	50	Adhesive grains with crack-like boundary	Fig. 5
5	1	100	Cracks formed	Fig. 6

Nd:YAG pulsed laser with 1062 nm wave length was used. Pulse duration varied from 0.1 to 100 μs and repetition rate was fixed at 100 Hz. For the oxidation of Cr film, the samples were mounted on a computer controlled X–Y stage to allow its movement under the laser beam with pre-set scan velocity. Typically, laser beam under focus on the sample surface turned into a 1-mm diameter spot by 100 mm focal length lens with laser energy density from 20 to 100 mJ/cm^2 in air. Typical laser irradiation parameters used in the present study are given in Table 1.

Surface morphology was studied with a SEM, JSM-5310. An Au layer ~100 Å thick was deposited on every sample by ion sputtering for the improvement of electric conductivity for SEM observation. Microstructure and stress analysis were performed by XRD measurements with a D8 Discover diffractometer ($\lambda = 0.154$ nm). Cr films were analyzed by XRD in normal mode. After pulsed laser irradiation, low-angle scan mode was performed to limit X-ray penetration depth to the region near the oxide film surface.

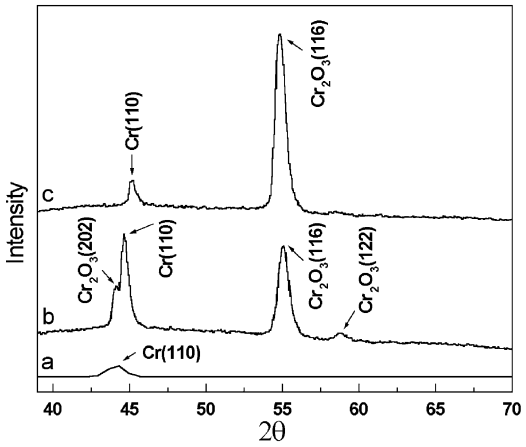

Fig. 1. XRD patterns of: (a) initial Cr film, in normal mode; (b) Cr film surface after laser irradiation at 100 μs pulse duration, laser density 20 mJ/cm^2, in low-angle scan mode; (c) Cr film surface after laser irradiation at 1 μs pulsed duration, laser density 30 mJ/cm^2, in low-angle scan mode.

3. Results and discussion

The initial Cr films deposited on glass was analyzed by XRD. It showed (Fig. 1. line a) that thermal evaporated Cr films grew and formed (1 1 0) texture since the surface energy was the smallest at the (1 1 0) plane in b.c.c. [7]. The grain size of Cr film calculated by integral width of XRD peak was about 13.4 nm.

After pulsed laser irradiation at 0.1 μs, 100 mJ/cm^2 in air, surface morphology showed that isolated 20–100 nm Cr spots formed (Fig. 2), but no oxide formed. In this condition, pulsed laser

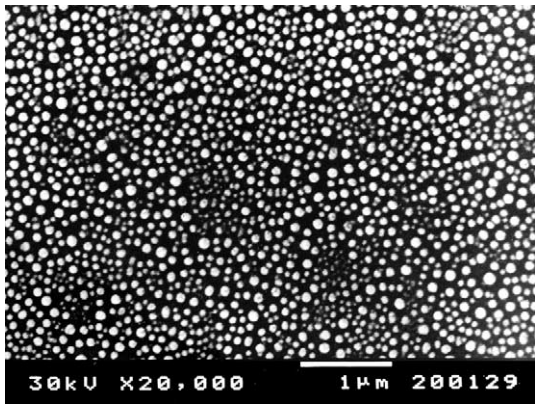

Fig. 2. Surface SEM image of nanocrystalline film by pulsed laser irradiation, 20–100 nm sized spots formed, laser density 100 mJ/cm^2, 0.1 μs pulse duration.

duration is too short to have enough time for Cr_2O_3 growth. The Cr film surface was merely fused and evaporated lightly and nanometer spherical spots formed because of both the short pulse duration and high cooling rate.

At the beginning of oxidation of Cr films, oxidation should primarily take place at both outer surface and at grain boundaries because oxidation is a diffusion controlled process. Diffusion in the outer surface and grain boundary (short-circuit diffusion) are much faster than that in the lattice [8]. When a 100 μs, 20 mJ/cm^2 pulsed laser was used, Cr_2O_3 film formed, which inherited the Cr film texture (Fig. 3). About 50 nm grain sized Cr_2O_3 film grew randomly along some planes such as (2 0 2), (1 1 6) and (1 2 2). The plane of Cr (1 1 0) can also be detected by the low-angle scan mode XRD (Fig. 1 line b). In this case, the longer pulse duration with the lower laser density should satisfy the conditions of near homogeneous growth of Cr_2O_3 grains. Based on a previous study about Cr_2O_3 formation at monocrystalline Cr (1 1 0) plane, the oxide grew in a fashion without orientation [9]. It can be similarly deduced that this type of oxidation mechanism also played the major role in oxidation with Cr (1 1 0) texture. As a result, the Cr_2O_3 film inherited the original Cr texture.

After moderate laser irradiation (1 μs, 30 mJ/cm^2) in air, surface morphology showed that dense and uniform 50–100 nm sized Cr_2O_3 (Fig. 4) film formed and only the Cr_2O_3 (1 1 6) plane was detected by XRD. The XRD result showed that in rapid oxidation, Cr_2O_3 growth from Cr (1 1 0) is along the (1 1 6) plane of Cr_2O_3. Under this case, because the outer surface diffusion is sufficiently faster than grain boundary diffusion, the oxidation process is controlled completely by grain boundary diffusion. Initial oxidation occurred only at the outer surface and grain boundaries. Furthermore, if growth of oxide is sufficient, the grain boundary could be pinned by oxide. The presence of this passivation layer on the surface of the film can inhibit further diffusion.

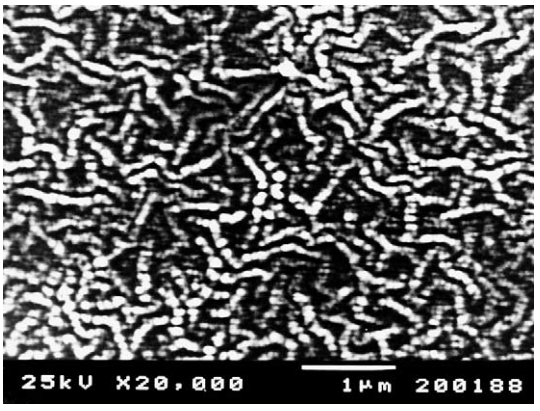

Fig. 3. Surface SEM image of nanocrystalline oxide film by pulsed laser irradiation, laser density 20 mJ/cm^2, 100 μs pulse duration. Oxide inherits Cr film texture.

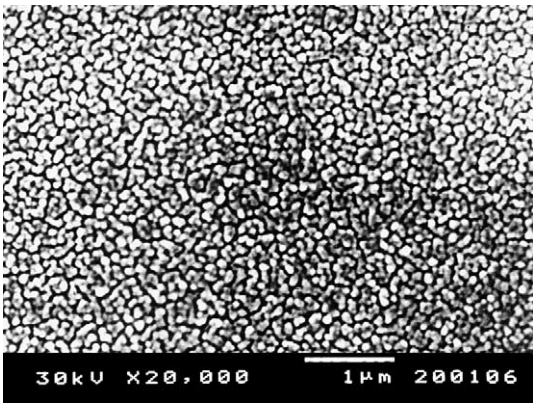

Fig. 4. Surface SEM image of nanocrystalline oxide film by pulse laser irradiation, laser density 30 mJ/cm^2, 1 μs pulse duration. Uniform 50–100 nm sized Cr_2O_3 surface film formed.

Our investigation also showed that after laser irradiation only Cr_2O_3 was detected by XRD while no other chromium oxide was found (Fig. 1). It differed from other research [10,11], in which Cu and Ti were oxidized by TGA and Nd:YAG laser, Cu_2O, Ti_2O_3 and TiO were found in addition to CuO and TiO_2. According to their discussion Cu_2O, Ti_2O_3 and TiO were the result of low temperature oxidation.

In an early paper by Renaud [12], XRD is not only a very powerful technique for quantitatively investigating the structures of surfaces and interfaces, but also very useful for providing information on the interfacial status for coherent interfaces or on the strain deformation. In our study, we found the Cr (1 1 0) peaks shifted (Fig. 1, line a, b and c). Indeed the 2θ (43.04° in line a) value in the initial Cr film was smaller than its corresponding

Table 2
Lattice parameters comparison of initial Cr film and Cr film after oxidation with Cr standard

Samples (as in Table 1)	XRD peaks of Cr (1 1 0)	2θ (°)	d_{110} (nm)	Contraction (%)	Internal stress
Initial Cr film	Fig. 1a	43.04	0.2099	−2.9	Tensile
Standard	XRD card	44.39	0.2039	0	Stress-free
2	Fig. 1b	44.65	0.2027	0.6	Compress
3	Fig. 1c	45.17	0.2005	2	Compress

value for a bulk Cr standard (44.39° in PDF card). After laser irradiation it was bigger (44.65° in line b and 45.17° in line c) than the standard. Values of d_{110} (lattice parameters) before and after laser oxidation were calculated by Bragg formula and summarized in Table 2.

In fact, in the initial Cr film tensile stress formed during Cr deposition and subsequent cooling with the glass substrate which was at 250 °C to improve adhesive ability at Cr/glass interface. The linear thermal expansion coefficient of Cr is 9.5×10^{-6}/°C is higher than that of the glass substrate (5.4×10^{-7}/°C). Due to this mismatch between the Cr film and substrate, larger shrinkage occurs in the Cr film than in the glass substrate and residual tensile stress will form after cooling.

Consequently during laser irradiation on sample 3 (Table 2), residual tensile stress in the initial Cr film will be relaxed by the formation of crack-like grain boundary wedge [13], which should be rapidly infilled by Cr_2O_3 growth. On the principle of Pilling–Bedworth ratio (PBR, the volume of oxide divided by that of the metal from which it is formed) [8], the PBR value of Cr is 2.07 which is much larger than 1. Therefore, the growing Cr_2O_3 can insert into crack-like grain boundary wedge zones, and the volume of Cr grain boundary will increase. Where Cr_2O_3 enwrapped Cr grains, the internal Cr grain should be compressed by growth stresses from Cr_2O_3. This insert effect could form a large compression on the unoxidized Cr core. In short, the growth stress from Cr_2O_3 was the main reason for lattice contraction.

For sample 2 (Table 2), because the internal oxidation in the Cr grain continued when pulse duration was longer, oxidation occurred uniformly in all Cr grains and grain boundaries, which will reduce the inhomogeneous growth stress. That is the reason lattice contraction is much lower in line b than in line c (Fig. 1).

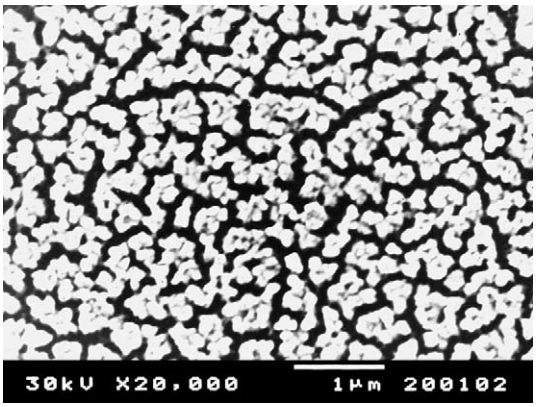

Fig. 5. Surface SEM image of nanocrystalline oxide film by pulsed laser irradiation, laser density 50 mJ/cm^2, 100 μs pulse duration; adhesive Cr_2O_3 grains were found.

If higher laser density irradiation (50 mJ/cm^2) was used, large grain sized adhesive Cr_2O_3 film formed (Fig. 5). This, in turn, resulted in large growth stress when adhesion and sintering developed among Cr_2O_3 grains. A crack-like grain boundary will form. For maskless non-photolithography process, laser induced Cr_2O_3 growth appeared only in areas where we relatively moved the laser beam (X–Y stage movement). When the chemical process (etching) was preformed, unoxidized and thus unprotective areas of Cr film were etched away, leaving behind the pattern of the laser movement. It is obvious that in this kind of film (Fig. 5), Cr exposed among the crack-like grain boundary will weaken the protection by Cr_2O_3 film. Only dense Cr_2O_3 film (Fig. 4) can protect Cr film from etching successfully [5]. In addition, in the dense oxide film (Fig. 4) the grain boundaries were pinned and sealed completely. The presence of this passivation layer on the surface of the film can inhibit further diffusion and oxidation. When the laser density is larger than 50 mJ/cm^2 (for example, 100 mJ/cm^2), the Cr film overheated. Large thermal stress formed and cracks (Fig. 6) occurred.

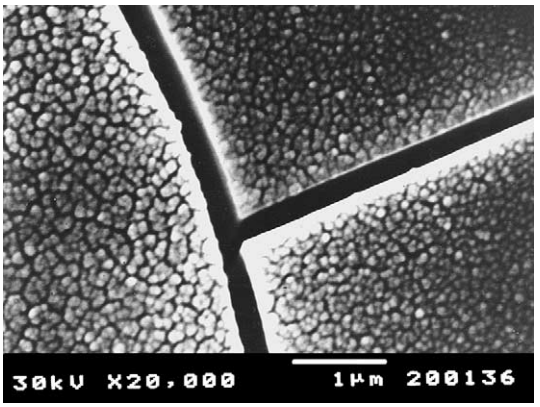

Fig. 6. Surface SEM image of nanocrystalline oxide film by pulsed laser irradiation, laser density 100 mJ/cm^2, 1 μs pulse duration; cracks formed.

4. Conclusions

In surface oxidation treatments of Cr films with Nd:YAG pulsed laser irradiation, it has been observed that in long pulse duration (100 μs) and low power density (20 mJ/cm^2) laser irradiation Cr_2O_3 grew near homogeneously, which did not damage the initial texture of Cr film. In short pulse duration (1 μs) and high power density (30 mJ/cm^2) laser irradiation, Cr_2O_3 growth preferred orientation along the (1 1 6) plane; The d_{110} lattice contraction of Cr film was produced beneath the oxide surface after pulsed laser irradiation. Internal growth stresses were considered as the reason for the lattice parameter contraction.

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