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Fluence dependence of femtosecond-laser-induced nanostructure formed on TiN and CrN

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ABSTRACT The fluence dependence of the nanostructure formation, which has been observed in our recent experiments on femtosecond (fs)-laser ablation, was examined in detail for hard thin films of TiN and CrN. The size D of the periodic fine structure formed with fs-laser pulses can be divided into two regions that depend on the laser fluence F, i.e. the region I where D increases rapidly with increasing F near the ablation threshold, and the region II where D increases slowly with an increase in F and almost saturates. The nanostructure has been observed only in the region I with a narrow width of F. The region II produces a periodic ripple structure whose size is 1/2–4/5 of the wavelength used. The effects of the thermal process and material composition on the nanostructure formation are discussed.

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1 Introduction

Ceramic coatings such as titanium nitride (TiN) and chromium nitride (CrN) have been extensively used as a variety of engineering materials to improve wear resistance, corrosion resistance, antiseizure properties and so on [1]. For example, these nitride coatings are employed for hardening surfaces of cutting tools and metal molds and also for decorating frames of glasses and watches with the gold color of TiN and the silver color of CrN. However, it is very difficult to mechanically process the coatings due to their high hardness and brittleness and also to remove them by means of chemical reactions. Thus, a new approach has been required for the purposes of microstructuring the hard thin films.

A high-intensity femtosecond (fs) laser has opened new possibilities for microstructuring of various materials, because of an ultra-short interaction duration and a resulting negligible heat-affected zone on the material surface. In our recent paper [2], we have demonstrated that very fine structures are formed on the thin-film surfaces of TiN and diamond-like carbon (DLC) by irradiating fs-laser pulses at an energy fluence slightly above the ablation threshold. The fine-structure formation strongly depended on the laser polarization and wavelength: the linearly polarized fs-laser pulses produced arrays of fine periodic structures oriented to the direction perpendicular to the laser polarization, while the circularly polarized fs pulses created fine dot structures; the size of these fine structures is 1/10–1/5 of the laser wavelength used and decreases with decreasing wavelength. The observed structure size was much smaller than that of well-known ripple structures often observed on laser-ablated material surfaces [3, 4]. It should be noted that we have produced a surface structure of several tens of nanometers on the thin films with ultraviolet (UV) fs-laser pulses at 267 nm.

Recently, Bonse et al. [5–7] reported several studies of the fundamental properties of microstructuring of the fs-laser-ablated TiN films coated on silicon substrates, as well as the chemical and morphological aspects.

In this paper, we report a systematic experimental study of the morphology change of film surfaces that are ablated with fs-laser pulses. In the present experiments, we have precisely controlled the laser fluence to make clear the experimental condition to form the nanostructure on the surfaces of hard coatings. We have observed that the nanostructure is also formed on CrN, as well as on TiN, and the experimental conditions for the nanostructure formation are compared for these two nitrides to see the effect of material composition. In our recent paper [8], we have reported the fluence dependence of a fs-laser-induced nanostructure on DLC films, being associated with the new finding of surface modification of DLC to glassy carbon (GC). The present experimental results demonstrate that precise control of surface morphology of hard coatings is possible with fs-laser pulses, so that the new nanotechnology should be used to create a hard surface having an optimum tribological property.

2 Experimental

The experimental apparatus and procedure are almost the same as those described in our recent paper [2, 8]. Briefly, the TiN and CrN films were coated on stainless steel plates of 1-mm thickness, utilizing an arc ion-plating system (Kobe Steel, Ltd.) which includes a modified ion source using a magnetic field for the guiding of the plasma stream and resulting reduction of the number of macroparticles in the deposited film. Using pure Ti and Cr as the cathode material, the TiN and CrN films were grown on the stainless steel plates with a bias voltage of 40 V and an arc current of 100 A in pure

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N_2 gas, respectively. These films were irradiated by intense fs-laser pulses from a Ti:sapphire chirped-pulse amplification system operated at a repetition frequency of 10 Hz. The fundamental 800-nm, 40-fs pulses were used to ablate the films. A half-wave plate was employed for rotating the linear polarization direction, and a quarter-wave plate for producing circular polarization. A fs-laser pulse with a pulse energy of 40–1100 μJ was focused on the films in air with a 100-cm-focal-length lens. The focal spot size on the target film was about 200 μm in diameter; the fluence on the target was then 0.1–3.0 J/cm^2. Depending on the fluence, a number of laser pulses of $N = 1–100$ was superimposed on the target.

With a field emission scanning electron microscope (SEM, Hitachi, Ltd., S-4100) and a scanning probe microscope (SPM, Seiko Instruments Inc., Nanopics 1000), we carefully examined the morphology change of the film surface that was ablated by the fs-laser pulses. The detailed characterization of the chemical bonding at the irradiated film surface was analyzed by small-spot X-ray photoelectron spectroscopy (XPS, Physical Electronics, Quantum 2000) with a spot size of about 100 μm.

3 Results and discussion

Table 1 summarizes the physical properties of the TiN and CrN hard coatings used for the present experiments.

Figures 1 and 2 show the SEM images around the center of TiN film surfaces ablated by the linearly and circularly polarized fs-laser pulses at different fluences, respectively, where $N = 100$ are used at low fluence ($F <\sim 0.9$ J/cm^2) and $N = 10$ at larger fluence. In Figs. 1a and 2a, the SEM images of non-irradiated film surfaces are also shown for comparison. The different pulse number N used for ablation is due to the fact that the ablation rate increases with an increase in the fluence F, and then $N = 100$ at $F >\sim 0.9$ J/cm^2 was observed to completely remove a part of the thin TiN film on the substrate. As seen in Fig. 1b, arrays of the periodic fine structure oriented almost to the direction perpendicular to the laser polarization are formed at such small fluences as $F = 0.15$ J/cm^2, just above the observed ablation threshold of $F \sim 0.14$ J/cm^2, as described below. The mean spacing D(s) of the fine structures is 130 nm and much smaller than the laser wavelength λ, as in our recent observations [2]. On the other hand, as seen in Fig. 2b, fine dot structures with a mean grain diameter $D(\varnothing)$ of about 110 nm are formed at $F = 0.15$ J/cm^2, just above the observed ablation threshold. As seen in Figs. 1 and 2, D(s) and $D(\varnothing)$ increase with an increase in F up to ~ 3.0 J/cm^2.

Figure 3 plots the mean spacing D(s) (a) and the diameter $D(\varnothing)$ (b) of the fine surface structure measured as a function of F. As indicated in this figure, D may be divided into two regions depending on F for convenience of discussion, i.e. one is the region I where D increases rapidly with increasing F near the ablation threshold, and the other is the region II where D increases slowly with an increase in F and almost saturates. The ratio D/λ is measured to be 0.15–0.3 in the region I, while D/λ is 0.5–0.8 in the region II. It has often been observed so far that a periodic surface structure called a rip-

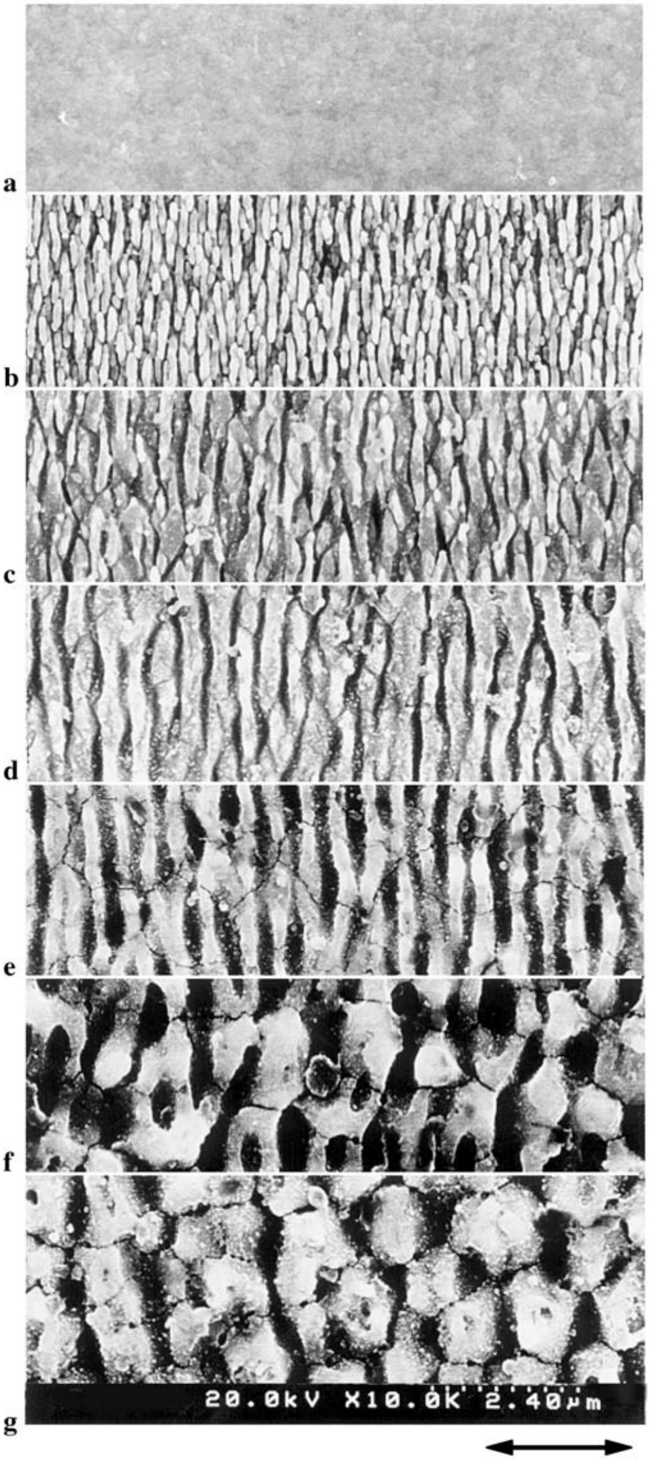

FIGURE 1 SEM images of non-irradiated TiN film (**a**) and those ablated by linearly polarized fs-laser pulses at $F = 0.15$ (**b**), 0.18 (**c**), 0.23 (**d**), 0.98 (**e**), 2.0 (**f**) and 3.0 J/cm^2 (**g**). $N = 100$ for (**b**)–(**d**) and 10 for (**e**)–(**g**). The *arrow* indicates the polarization direction of the fs-laser pulses

	TiN	CrN
Thickness [μm]	2	2.2
Hardness, Hv	2100	1900
Roughness, Ra [nm]	65	80

TABLE 1 Physical properties of the TiN and CrN hard coatings used in the experiments

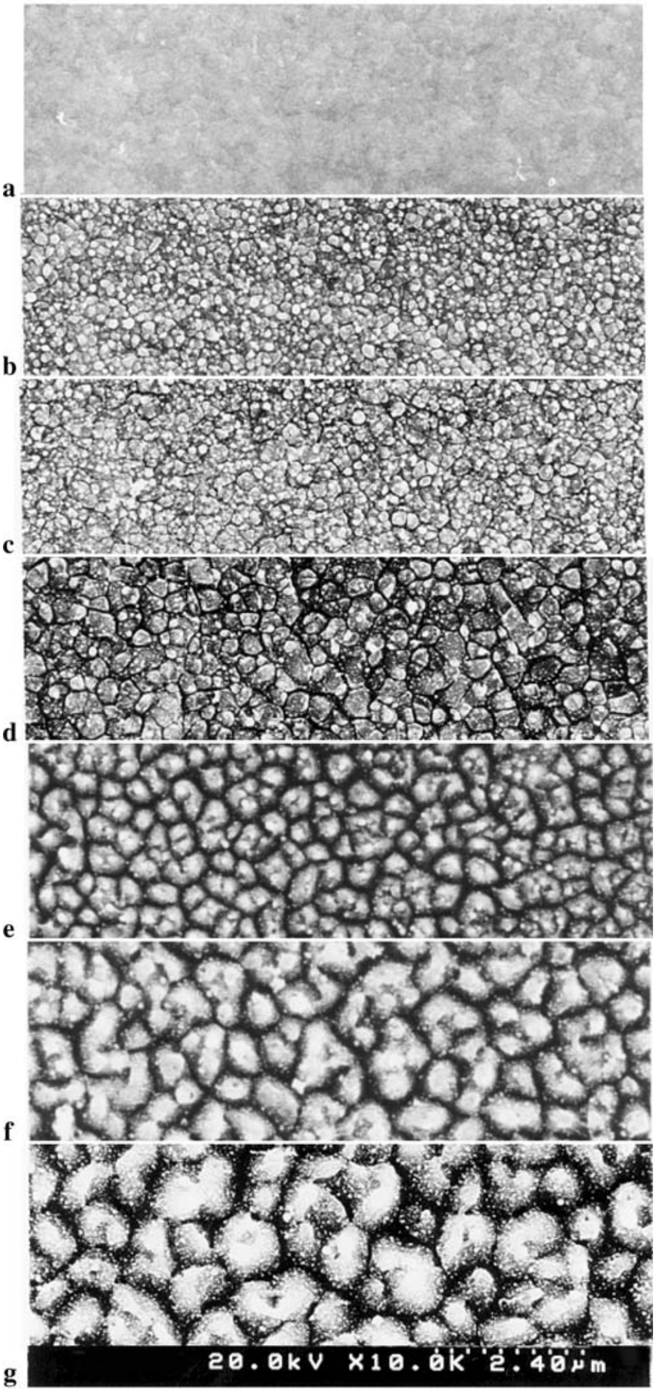

FIGURE 2 SEM images of non-irradiated TiN film (**a**) and those ablated by circularly polarized fs-laser pulses at $F = 0.15$ (**b**), 0.17 (**c**), 0.23 (**d**), 1.2 (**e**), 2.2 (**f**) and 3.1 J/cm^2 (**g**). $N = 100$ for (**b**)–(**d**) and 10 for (**e**)–(**g**)

ple is formed on the material surfaces ablated by the linearly polarized laser pulses [3, 4]. The size of the ripple spacing observed is of the order of the laser wavelength used; the ripple structure is then understood as a spatial structure produced by the interference between the incident laser light and the surface electromagnetic wave that is excited by the incident laser light. The mean spacing of the periodic structure formed in the region II in Fig. 3 almost corresponds to that of the ripple pattern, as well as the mean diameter of the dot structure formed with the circularly polarized light.

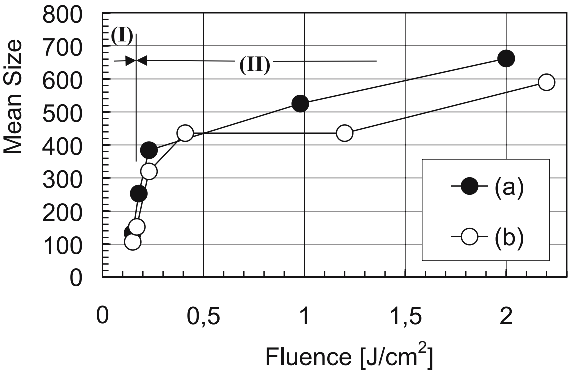

FIGURE 3 Fluence dependence of the mean spacing (**a**) and diameter (**b**) of periodic fine structures formed on TiN surfaces with linearly (**a**) and circularly (**b**) polarized fs-laser pulses

To see the macroscopic characteristics of ablation in the region I and determine an accurate ablation threshold, we measured with the SPM the cross-sectional crater profiles around the center of TiN film surfaces irradiated by the linearly polarized pulses at different fluences. The results for $F = 0.15$–$3.0\,\mathrm{J/cm^2}$ are shown in Fig. 4, where $N = 100$ for (a) and (b) and $N = 10$ for (c) to (e). The diameter and depth of the crater increase with an increase in F. In Fig. 5, the ablation rate L per laser shot that is deduced from the measured ablation depth is plotted as a function of the laser fluence. The ablation rate L can be well expressed by the relation [9]

$$L = 1/\alpha \ln(F/F_{\mathrm{th}})\,, \tag{1}$$

where α is the optical absorption coefficient and F_{th} is the threshold fluence for ablation. In Fig. 5, the straight solid line shows the least-squares fit by eq. (1). From the fitted line, we have the optical penetration depth of $1/\alpha \sim 34\,\mathrm{nm}$ and the threshold fluence of $F_{\mathrm{th}} \sim 0.14\,\mathrm{J/cm^2}$. The threshold fluence

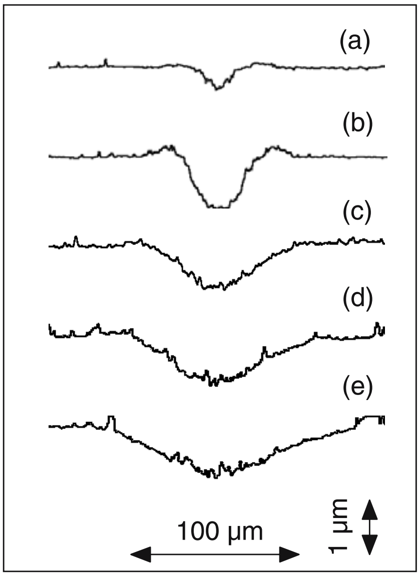

FIGURE 4 Crater profiles on TiN surfaces ablated by fs-laser pulses with linear polarization at $F = 0.15$ (a), 0.18 (b), 0.98 (c), 2.0 (d) and 3.0 J/cm^2 (e). $N = 100$ for (a) and (b) and 10 for (c)–(e)

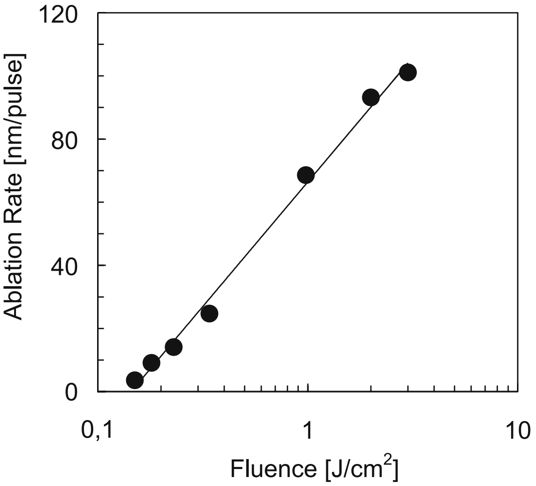

FIGURE 5 Fluence dependence of the ablation rate for TiN with linearly polarized fs-laser pulses

deduced is in excellent agreement with the value reported so far [6]. Comparing F_{th} with the results shown in Fig. 3, we may conclude that the region I to provide the nanostructure is in a narrow fluence range of $F/F_{\mathrm{th}} <\sim 1.2$. The ablation rate L at the fluence of 0.15 J/cm^2 in this region I shows a very small value of 3.6 nm per pulse. This value is one order smaller than that of the optical penetration depth.

In the region I discussed above, we suppose that the non-thermal process plays an important role for the nanostructure formation [11]. To see the change in the TiN chemical state induced by the fs-laser pulse, we measured XPS spectra of the laser-irradiated area with a spot size of about 100 µm. The results have shown that TiO_2 is formed in the film surface by the irradiation of fs-laser pulses in air. The oxidation rate at the surface was very small at F around the ablation threshold, as expected from the non-thermal interaction [11, 12]. However, we could not see any clear and/or chemical difference in the oxidation between the regions I and II, while the degree of oxidation was observed to increase with an increase in F.

We have also observed the nanostructure formation on the CrN film surface. CrN has a bonding structure similar to that of TiN but has some different physical properties. Figure 6 shows the SEM images around the center of CrN film surfaces ablated with $N = 100$ of the linearly polarized fs pulses at different fluences of $F = 0.11$ (b), 0.12 (c), 0.15 (d) and 0.25 J/cm^2 (e), where the SEM image (a) of a non-irradiated CrN film surface is included for comparison. The periodic structures are oriented almost to the direction perpendicular to the laser polarization, and the size of the structures increases with an increase in F. The mean spacing D(s) for the fine structure observed at the lowest fluence $F = 0.11$ J/cm^2 is measured to be 110 nm. It is noted that D(s) increases to 410 nm at a slightly higher fluence of $F = 0.12$ J/cm^2. With a further increase in F, D(s) increases very slowly and saturates. Figure 7 plots the measured D(s) of CrN as a function of F. Similar to the case of TiN, D for CrN can also be divided into the regions I and II, and the ratio D/λ is 0.14 in the region I while D/λ is 0.5–0.7 in the region II. It is noted in Fig. 7 that D for CrN increases much more rapidly than that for TiN with an increase in F in the region I, i.e. the region I for CrN is very narrow. This fast increase in D in the region I may be attributed to the low melting temperature of CrN. It is known that CrN is decomposed at a lower temperature of about 1500 °C, while the melting point of TiN is 2950 °C [10].

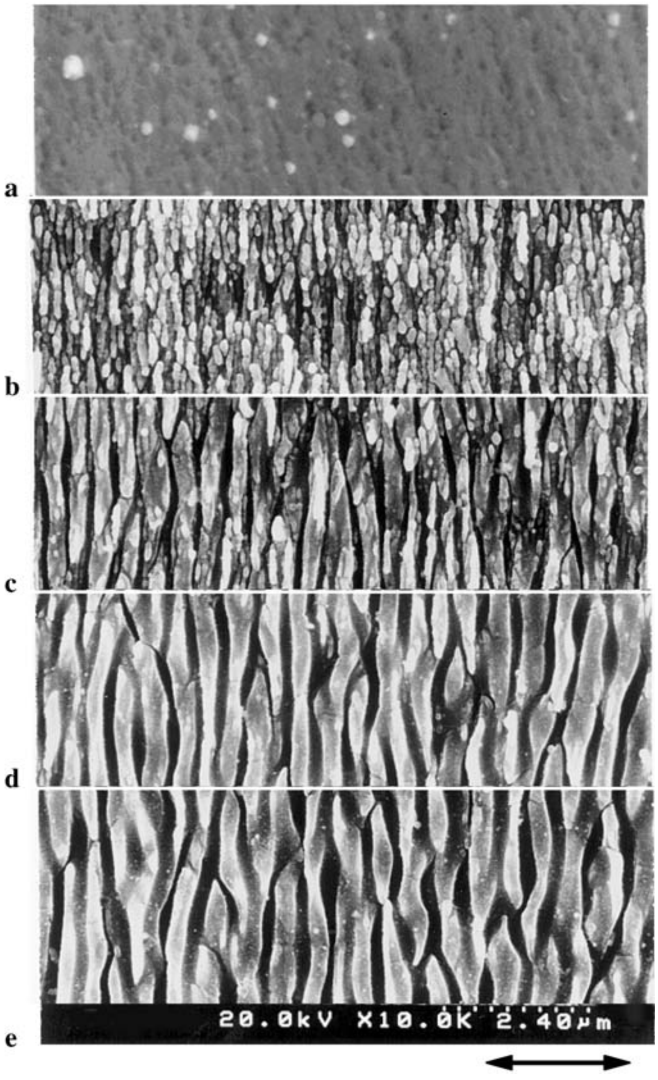

FIGURE 6 SEM images of non-irradiated CrN film (**a**) and those ablated with $N = 100$ linearly polarized fs-laser pulses at $F = 0.11$ (**b**), 0.12 (**c**), 0.15 (**d**) and 0.25 J/cm^2 (**e**). The *arrow* indicates the polarization direction of the fs-laser pulses

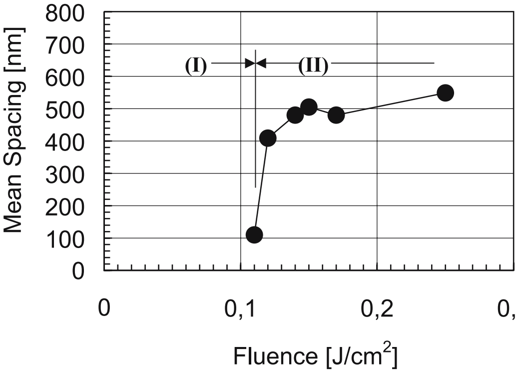

FIGURE 7 Fluence dependence of the mean spacing of periodic fine structures formed on CrN surfaces with linearly polarized fs-laser pulses

Furthermore, from the point of view of the formation free energy [10], the thermal stability of CrN would be lower than that of TiN. Thus, CrN should be more sensitive to the laser fluence than TiN, resulting in the low ablation threshold of $F \sim 0.10\,\mathrm{J/cm^2}$.

The above results suggest that the nanostructure formation strongly depends on the intrinsic thermal properties of each material, and the non-thermal interaction process appears to be essential to form the nanostructure on the hard coatings, being consistent with our recent results [11]. In fact, for stainless steel, having a lower melting point than nitrides, we have observed that the periodic nanostructure is formed only in a low-fluence area on the periphery of a fs-laser-irradiated spot.

4 Conclusion

We have made an experimental study of the fluence dependence of fs-laser-induced nanostructure formation on hard thin films of TiN and CrN and discussed the detailed experimental conditions for the nanostructure formation. The results are summarized as follows.

1. The size D of the periodic structure formed by irradiating fs-laser pulses is divided into two regions of the laser fluence F, i.e. one is the region I where D increases rapidly with increasing F near the ablation threshold, and the other is the region II where D increases slowly and almost saturates.
2. The nanostructure is formed only in the region I, which is very narrow and expressed by $F/F_{\mathrm{th}} <\sim 1.2$ for TiN.
3. The experimental condition for nanostructure formation is closely associated with the thermal properties of the materials, and the importance of a non-thermal process is suggested for the nanostructure formation in the region I.
4. The ablation threshold for CrN is smaller than that of TiN, and the fluence region for nanostructure formation on CrN is extremely narrow compared with that for TiN.

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