Ordered YBCO sub-micron array structures induced by pulsed femtosecond laser irradiation

C. W. Luo,[1*] C. C. Lee,[1] C. H. Li,[1] H. C. Shih,[1] Y.-J. Chen,[1] C. C. Hsieh,[1] C. H. Su,[1] W. Y. Tzeng,[1] K. H. Wu,[1] J. Y. Juang,[1] T. M. Uen,[1] S. P. Chen,[2] J.-Y. Lin,[3] and T. Kobayashi[4]

[1]*Department of Electrophysics, National Chiao-Tung University, Hsinchu, Taiwan, R.O.C.*

[2]*Advanced Energy Technology Laboratory, ERL, ITRI, Chutong, Hsinchu, Taiwan, R.O.C.*

[3]*Institute of physics, National Chiao Tung University, Hsinchu, Taiwan, R.O.C.*

[4]*Department of Applied Physics and Chemistry and Institute for Laser Science, The University of Electro-Communications, Chofugaoka 1-5-1, Chofu, Tokyo 182-8585 Japan*

[*]*Corresponding author: cwluo@mail.nctu.edu.tw*

Abstract: We report on the formation of organized sub-micron $YBa_2Cu_3O_7$ (YBCO) dots induced by irradiating femtosecond laser pulses on YBCO films prepared by pulse laser deposition with fluence in the range of 0.21∼0.53 J/cm^2. The morphology of the YBCO film surface depends strongly on the laser fluences irradiated. At lower laser fluence (∼0.21 J/cm^2) the morphology was pattern of periodic ripples with sub-micrometer spacing. Slightly increasing the laser fluence to 0.26 J/cm^2 changes the pattern into organized sub-micron dots with diameters ranging from 100 nm to 800 nm and height of 150 nm. Further increase of the laser fluence to over 0.32 J/cm^2, however, appeared to result in massive melting and led to irregular morphology. The mechanism and the implications of the current findings will be discussed. Arrays of YBCO sub-micron dots with T_c = 89.7 K were obtained.

OCIS codes: (140.3390) Laser materials processing; (220.4241) Nanostructure fabrication; (160.0160) Materials

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1. Introduction

The worldwide efforts devoted in developing nanotechnologies over the last decade have undoubtedly flourished tremendous impact in modern industrial applications and in basic science researches. For the so-called top-down approaches used in fabricating nanostructures or devices, photolithography and chemical etching have been the widely adopted combination. However, the size of structures obtained with this approach is restricted by the diffraction limit of the light source used. Furthermore, the chemicals frequently used in chemical etching have raised serious environmental concerns. Recently, significant progress in overcoming the diffraction limit has been realized by the near-field lithography (NFL)[1]-[3]. Ohtsu et al.[1] were able to produce a structure with 160 nm pitch and sub-50 nm width, both are smaller than the wavelength of the light source (λ = 365 nm). Even though the NFL is capable of reaching resolution order of magnitude smaller than the wavelength of the exposure light source, fabrication of complicated masks and extremely accurate alignment procedures are needed.

On the other hand, since the introduction of femtosecond laser amplifiers, nanoscale microstructures on the surface of materials have been demonstrated by irradiating the surface with an 800 nm femtosecond laser. It is generally believed that the formation of the ripple-like periodic structures generated by a single laser beam on the surface of various materials[4]-[16] is primarily due to the interference between the incident pulses and that scattered from defects on the surface[15]. Furthermore, other nanostructures, e.g. tungsten nanospikes[5], titanium nanocones[16] have also been created by 800 nm femtosecond laser pulses. These results clearly demonstrated that femtosecond laser can be a viable tool in obtaining nanostructures even with organized patterns by simply irradiating the surface of the targeted materials. In this report, we demonstrate that, with properly chosen fluences, organized patterns of the high-T_c superconductor $YBa_2Cu_3O_7$ (YBCO) sub-micron ripples and sub-micron dots can indeed be obtained by femtosecond laser irradiation, while keeping the composition and properties of the original films essentially unchanged.

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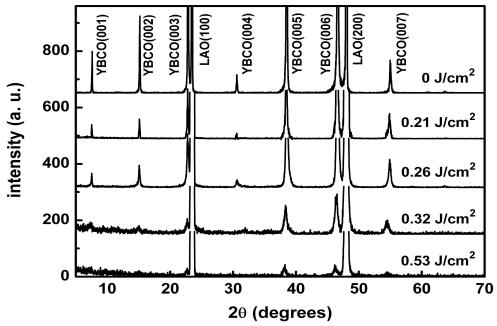

Fig. 1. XRD signals of YBCO thin films at various laser fluences.

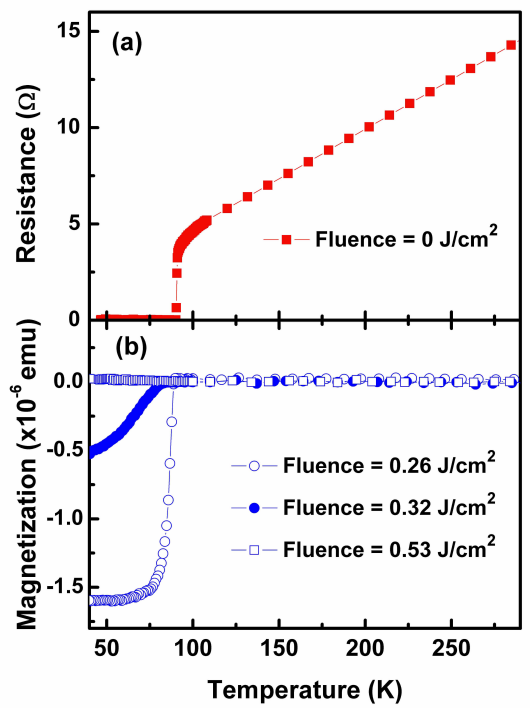

Fig. 2. (a) The resistance versus temperature curve measured before femtosecond laser irradiation (fluence = 0 J/cm^2). (b) The magnetization versus temperature curve measured at 10 Oe after femtosecond laser irradiation with various fluences (0.26 ~ 0.53 J/cm^2).

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2. Experiments

The YBCO samples used in this study were prepared by pulse laser deposition with a 248 nm KrF excimer laser operating at a repetition rate 3-8 Hz and an energy density of 2-4 J/cm^2. The laser beam with 25 ns pulse duration was focused on the target surface with a spot size of 1 mm $\times$ 3 mm by a lens. The target-substrate distance was fixed to 4.5 cm with an on-axis deposition geometry. The oxygen partial pressure during deposition was maintained at 0.25 Torr. The substrate temperature was kept at 780-790 ^{o}C. After the completion of deposition, the film was cooled to room temperature under 600 Torr of oxygen with the heater off. The thickness of the film was about 200 nm. As is evident from the top x-ray diffraction (XRD) pattern shown in Fig. 1, the YBCO films were (001)-oriented normal to the (100) orientation of the $LaAlO_3$ (LAO) substrate. The temperature-dependent resistance of an (001)-oriented YBCO thin film was measured by the standard four-probe configuration as shown in Fig. 2(a). The resistance decreases linearly with temperature in the normal state and then drops sharply to zero-resistance superconducting state at 90.1 K. Both features are consistent with the x-ray diffraction (XRD) result that indicates the high quality of the YBCO films. Fig. 3(a) shows the surface morphology of the typical (001)-oriented YBCO films scanned by ultra-high resolution field emission scanning electron microscope (FEG-SEM, JOEL JSM-7000F). The image again depicts the high quality of the YBCO thin films used in this study.

A commercial regenerative amplified Ti:sapphire laser (Legend USP, Coherent) with 800 nm wavelength, 35 fs pulse duration, $\sim$ 0.5 mJ average energy, and 5 kHz repetition rate was used as the irradiation source. After passing through a variable neutral density filter, the beam was two-dimensionally scanned by a pair of galvanic mirrors with a speed of 7.6 cm/s. An f-theta lens with focal length of 19.6 cm and numerical aperture of 0.18 was used to focus the laser beam on the sample. By the knife-edge method, the spot size of 110 μm (full width at half maximum) on the sample surface was measured. For this spot size, the overlap of the pulses during scanning a line is around 86% and the off-set between the lines is $\sim$85 μm. All experiments were performed in air under atmospheric pressure. The fluence of the laser beam was estimated by measuring the power at the entrance of the scanner system divided by the repetition rate and the irradiated area(=spot size on the sample surface, which is irradiated with 22 pulses). The surface morphology of femtosecond laser-induced surface modifications was inspected by using SEM and atomic force microscope (AFM). The composition of samples was analyzed by the energy dispersive spectroscopy (EDS, Oxford instruments) attached to the SEM system.

3. Results and discussion

It is evident from Fig. 1 that the crystalline structure of the YBCO films remains high quality after irradiated by the femtosecond laser with fluence up to 0.26 J/cm^2. However, it deteriorates significantly with further increase of laser fluence. For instance, with an irradiation fluence of 0.53 J/cm^2, the intensity of the characteristic x-ray diffraction peaks is nearly diminished. In addition, the superconductivity of the irradiated samples is difficultly identified by the resistance measurements as the untreated sample in Fig. 2(a) due to the rougher surface or separated dots, which can be overcome by the magnetization measurements. As shown in Fig. 2(b), while the superconductivity of the YBCO films remains almost unchanged under low fluence irradiations, it starts to degrade at an irradiation level of 0.32 J/cm^2 and completely lost at 0.53 J/cm^2, indicating that there are some structural and compositional changes involved at higher irradiation fluences. We will come back to these with the EDS results.

Perhaps, the most dramatic effect induced by the femtosecond laser irradiation is the changing of the surface morphology of the YBCO films. Fig. 3(b)-(e) clearly depict the dramatic change of the resultant surface morphology as a function of the irradiating fluence of the fem-

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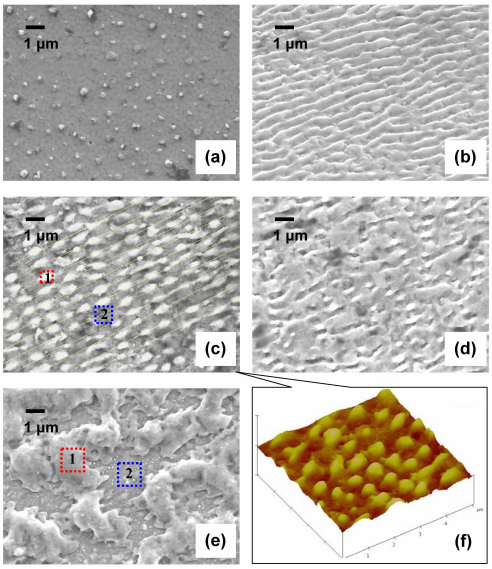

Fig. 3. SEM images show the surface morphology of YBCO thin films at various laser fluences. (a) Fluence = 0 J/cm^2 (b) Fluence = 0.21 J/cm^2 (c) Fluence = 0.26 J/cm^2. The solid lines are a guide to the eye emphasizing the alignment of YBCO nanodots. (d) Fluence = 0.32 J/cm^2 (e) Fluence = 0.53 J/cm^2 (f) AFM image of (c).

tosecond laser. As shown in Fig. 3(b), for a laser fluence of 0.21 J/cm^2, the morphology of the film structure was modified from a flat surface to organized subwavelength ripples. It is also interesting to note that the orientation of the ripples is perpendicular to the polarization direction of the linearly polarized laser beams. Furthermore, the "periodicity" of the ripple-like structures is approximately 500 nm, which is much smaller than either the wavelength or the spot size of the femtosecond laser, indicating that the pattern is not formed by simple plow-and-deposit processes. In fact, similar results have been observed by irradiating laser pulses on metals[4]-[6], semiconductors[4][7]-[11], and insulators[12, 13]. The origin of these irradiation induced organized pattern formation is believed to result from the inhomogeneous energy input across the ablating spot due to the interference between the incident beam and the microscopic fields scattered by a surface roughness[13]-[15]. As a result, the orientation and periodicity of the ripples are sensitively dependent on the polarization, angle of incidence, fluence, wavelength and the number of pulses. For a linearly polarized laser light, the periodicity D of the laser-induced periodic surface structures is given by[15]

$$D = \lambda / (1 \pm sin\theta)$$

Where λ is the wavelength of the incident light, θ is the angle of the incidence with respect to the surface normal. In the current study, the periodicity of D is estimated to be around 773 nm with $\theta \sim 2^\circ$. However, as the fluence of the laser beam was raised to 0.26 J/cm^2, the ripple structure displayed in Fig. 3(b) appears to be interrupted and turns into organized sub-micron

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dots (Fig. 3(c)). The height and diameter of the sub-micron dots are 150 nm and 100 $\sim$ 800 nm, respectively, as revealed by the AFM image shown in Fig. 3(f) and the SEM image shown in Fig. 3(c). All of the YBCO sub-micron dots align regularly along the direction perpendicular to the polarization of irradiated light (the solid lines in Fig. 3(c)).

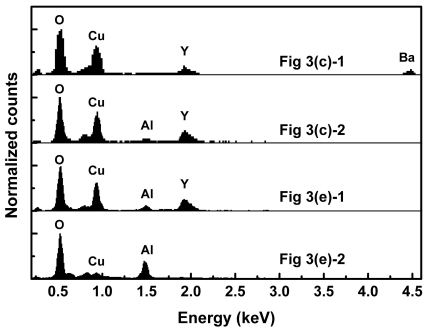

Fig. 4. EDS spectra show the composition of area 1 and area 2 in Fig. 3(c) and Fig. 3(e).

As has been mentioned above, the crystalline structure of these YBCO sub-micron dots induced by the laser irradiation (0.26 J/cm^2) remains *c*-axis oriented with a sharp diamagnetic Meissner effect characteristics at 89.7 K (Fig. 2(b)), indicating that even after the dramatic morphology reconstruction the obtained sub-micron dots still keep most of intrinsic properties intact. Indeed, as indicated by the top EDS spectrum displayed in Fig. 4 which was taken on one of the sub-micron dots (marked as area 1 in Fig. 3(c)), the composition of the sub-micron dot does not change from that of the original YBCO films. The EDS results taken in the area between the dots (marked as area 2 in Fig. 3(c)) indicate that there is no signal of Ba. Instead, trace of Al, presumably coming from the LAO substrate, was detected (see the second spectrum from the top in Fig. 4). This result indicates that the composition in the area between any two sub-micron dots has severely deviated from the stoichiometric composition of original YBCO. The question is how does it occur?

Due to the laser pulses, the transient increase in temperature, ΔT, for materials can be estimated by using the following relation

$$\Delta T = W/CV$$

where W is the pulse energy, C is the heat capacity, and V is the illuminated volume. For YBCO at 300 K using $C = 2.86\times10^6$ J/m^{3}K[17], V = 1.14×10^{-14} m^3 (the absorption length $\sim$ 80 nm and a spot size of 110 μm), and W in the order of 0.1 mJ. ΔT is approximately 3000 K. This temperature increase, in principle, will lead to massive global melting of thin layer beneath the surface of YBCO thin films. Thus, a more random pattern is expected when re-solidified. However, due to the interference induced by the inhomogeneous input energy, at first, the YBCO in melted phase forms the ripple according to the interference pattern which pushes the YBCO to the line of destructive interference. This interference pattern also leads to a periodic distribution of the temperature fluctuation, ΔT, which happens to be higher than the boiling point of Ba (1897 K[19]) along the line of constructive interference and lower than the boiling point of Ba along the line of destructive interference. As a result, in the regions of the constructive interference most Ba was vaporized, while those in the destructive regions remain. Moreover, due to the surface tension, the melted YBCO undergoes heterogeneous nucleation

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on the substrate surface along the lines of destructive interference and aggregates to form sub-micron dots in a periodic fashion, as shown in Fig. 3(b)-(c) and 3(f). The present results suggest that, by using a single-beam femtosecond laser irradiation, it is possible to fabricate a self-organized array of YBCO sub-micron dots with most of the crystallinity and superconducting properties remaining intact, provided proper control of irradiation fluence is practiced. This technique, thus, may be potentially applied to the fabrication of the microwave filter devices with array structure or the weak-link Josephson junction arrays.

Finally, as the fluence reaches $\geq$ 0.32 J/cm^2, the irregular and disordered patterns are observed on the surface of the LAO substrate as shown in Fig. 3(d) and Fig. 3(e). The characteristic XRD peaks of the (001)-YBCO films deteriorated significantly (Fig. 1), indicating that the crystalline structure of YBCO has been destroyed by the higher laser fluences. The EDS analysis (Fig. 4) also shows that Ba is missing in both area 1 and area 2 marked in Fig. 3(e). In area 2, even the composition of Y is missing in the EDS spectrum. Using the previous estimation with $W \geq 0.12$ mJ (fluence $\geq$ 0.32 J/cm^2), $\Delta T \geq 3700$ K is obtained, which is higher than the boiling point of Ba (1897 K[19]) at both positions of constructive and destructive interference but is only higher than the boiling point of Y (3345 K [19]) at the position of constructive interference. In this case, the aggregation of the melted YBCO becomes more disordered and the stoichiometric composition is more severely influenced leading to the loss of crystalline integrity and superconductivity in the remaining residue of the original YBCO film.

4. Summary

In summary, we have demonstrated that the surface microstructure of YBCO thin films can be manipulated by properly controlling the fluence of the irradiating femtosecond laser. With a fluence of 0.21 J/cm^2, a ripple pattern was clearly observed on the surface of one YBCO thin film. After raising the laser fluence to 0.26 J/cm^2, the (001)-YBCO film turns into (001)-sub-micron dot array with the superconductivity remains almost intact (T_c = 89.7 K as compared to 91 K for the original film). These sub-micron dots structure and superconductivity, however, were rapidly destroyed with fluence higher than 0.32 J/cm^2. The present results clearly demonstrate that the femtosecond laser, in addition to be crucial in studying the ultrafast dynamics, can also serve as a new way of engineering the material surfaces into nanometer scale structures.

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