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COLORATION EFFECT OF PULSED LASER ON WO_3

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When laser pulses irradiate the surface of the sample WO_3, an interesting coloration effect is obtained. Only by one pulse of XeCl laser irradiation (wavelength: 308 nm, pulse duration: 36 ns, output power: 100 mJ/pulse), a significant color change appears. X-ray photoelectron spectroscopy (XPS) shows that a partial reduction process of WO_3 occurs and conduction band electrons appears. X-ray diffraction pattern indicates that the lattice parameters of the colored samples are increased. A molten layer can be seen in scanning electron microscopy (SEM) image. It may be concluded that the coloration effect of pulsed laser undergoes a process different from that of electro- or photo- chromism, and may be attributed to thermochromism and substoichiometric WO_3 is formed. The coloration process is characterized by its high speed and stability.

PACC: 7870; 7280G; 4260K

I. INTRODUCTION

WO_3 has many significant semiconducting ferroelectronic and catalytic behavior, most of which are related to its structure that can be considered as a distortion of the cubic ReO_3 structure. All the metal atoms are surrounded by six oxygen atoms in an octahedral coordination, WO_3 are formed by sharing the vertices of the octahedral. Some small cations, such as, H^+, Li^+, Na^+, can be added continually to the hollow cubic to form tungsten bronze $M_xWO_3(0 < x < 1)$[1] with fixed color. As it can be used as large screen display, clever window, color registration etc, the study of electrochromism of WO_3 received widely consideration.[2,3] WO_3 may also be turned to blue color by long-time irradiation of ultraviolet light, which is termed as photochromism.

The process of electro- or photo- chromism is usually described in term of double-charge-injection model. In the process of photochromism[4], water is decomposed into H^+ and highly reactive O atoms upon irradiation of ultraviolet light, and H_xWO_3 forms. The interior or adsorbed water plays an important role. Another feature of photochromism is that time of color change as long as several hours to several days are needed to get notable coloration.

Here we present our research on the coloration effect of pulsed laser on WO_3, which is different from ordinary photochromism induced by ultraviolet light.

II. EXPERIMENTAL

A XeCl excimer laser was used as the irradiation source with wavelength of 308 nm, pulse duration of 36 ns, output power of 100 mJ/pulse. The laser was focused at the sample surface to an area of 6 mm×12 mm and power density as high as 3.88×10^6 W/cm^2 was obtained.

Commercial WO_3 powder was pressed into pellets which are of diameter of 14 mm. After annealing at 700 ℃ for 2 hours, density of the pellet was 4.77 g/cm^3.

Upon one irradiation of pulsed laser, remarkable color alteration was noticed, and was determined by UV-visible spectroscopy. The properties of the samples were studied by a RIBER LAS-3000 MK-2 XPS spectroscopy (using AlK α line as the X-ray source) and a JEM-630 1F Cold Emission Scanning Electronic Spectroscopy (SEM).

Ⅲ. RESULTS AND DISCUSSION

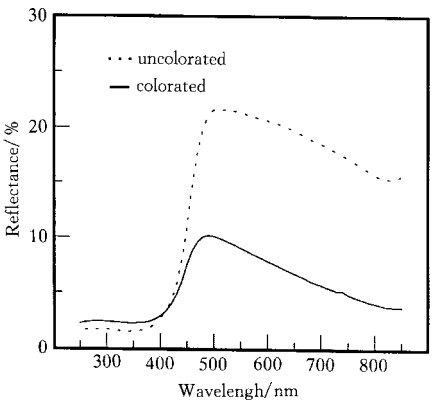

Fig.2. UV-visible diffuse reflectance of the fresh samples and the colored samples induced by pulsed laser

Fig.1. Photograph of WO_3 samples before (a) and after (b) irradiation of pulsed laser

As shown in Fig.1, the irradiation of pulsed laser changes the color of the WO_3 samples from yellow to blue and the UV-visible diffuse reflectance (Fig.2) show that the spectra of the colored and uncolored samples exhibit the identical features. In the UV region, with a wavelength shorter than 380 nm that is the fundamental absorption edge of WO_3, the samples show low reflectance. As the wavelength became longer, reflectance grows rapidly up to the highest value around 480 nm, and then begins to decrease smoothly. On the shorter wavelength region (<410 nm), the reflectance of the colored samples (irradiated by one laser pulse) is a little higher than that of the fresh samples. At the longer wavelength region (>410 nm), the reflectance of the colored samples is much lower than that of the uncolored one.

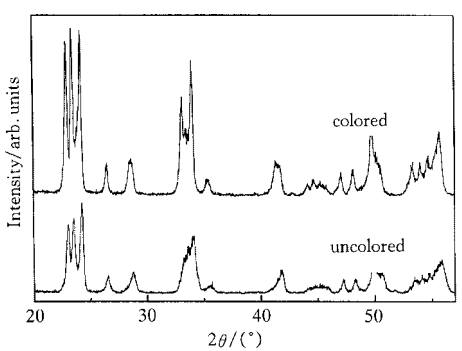

Fig.3. XRD patterns of fresh sample and the colored sample induced by pulsed laser

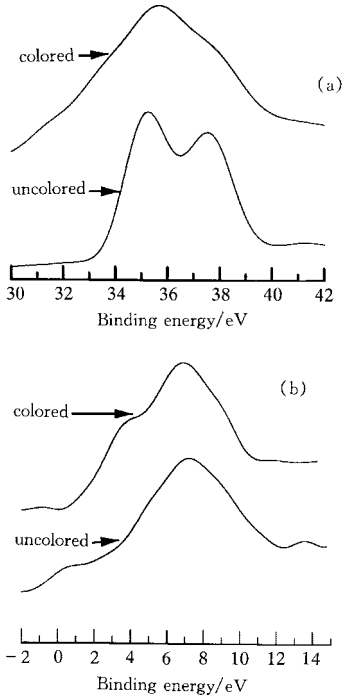

Fig.4. XPS spectra of the fresh and the colored samples induced by pulsed laser

The XRD patterns of the colored and uncolored samples are shown in Fig.3. Comparing with fresh samples, the XRD patterns of colored one shift to the direction of small angle. By calculating, the fresh samples are triclinic WO_3 with lattice constants a=7.292, b=7.523, c=7.683 which are approximate to the data on JCPDS 32-1395. The crystallographic axes of the colored samples are a=7.315, b=7.548, c=7.707 which become longer in three directions.

The XPS spectra of W4f of fresh samples are shown in Fig.4. The two peaks centered at the binding energy (BE) of 35.4 and 37.5 eV, represent $4f_{7/2}$ and $4f_{5/2}$ of W^{6+} respectively. When the sample was colored by irradiation, the spectrum becomes rather complex. Some additional peaks are noticed, which form the shoulder at the lower binding energy side and obliterates the valley of the original doublet. This may be caused by the creation of oxidation state W^{5+} with different binding energy from W^{6+}. The spectrum in the valence band region (Fig.4b) shows that an additional peak corresponding to W5*d* electrons appeared around 3 eV and these electron may stem from the conduction band.

Before irradiation, the sample surface is rough and porous as shown in the SEM image in Fig.5a. After only one pulse of laser irradiation, the surface of the colored sample except for some fractures becomes rather smooth as shown in Fig.5b. When the samples are bleached at 400 ℃ for 0.5 h, the surface (Fig.5c) becomes nearly the same as the colored one.

The above results mean that the topography changes are not the cause for coloration. The coloration may be interpreted as the changes in electronic structure that changes the properties of the photon absorption of samples. This has been demonstrated by the XPS spectra in Fig.4, which indicates the occurrence of W^{5+}, and the electron movement between W^{5+} and W^{6+} may cause the photon absorption to change.

As H_xWO_3 has large negative values of the Gibbs free energy associated with the oxidation process, the colored samples induced by ordinary ultraviolet light are so unstable that they would bleach gradually in air, and when they are in contact with H_2O_2[5,6], they lose their color immediately. On the contrary, the colored state induced by pulse laser irradiation is stable at 300 ℃ for 20 hours even being in contact with H_2O_2.

When annealed at above 350 ℃ in vacuum, WO_3 would be colored as stable substoichiometric WO_{3-x} for lose of oxygen[7]. As the photon energy of XeCl pulsed laser with wavelength of 308 nm (4.03 eV) is larger than the band gap of WO_3 (3.25 eV), laser photons

are absorbed by the surface of the sample, which are raised to high temperature state in several ns. As show in fig.5, upon irradiation of laser pulses, the surface temperature is higher than the melting point but lower than the boiling point of WO_3, so a molten layer is formed and the pores on the surface are filled. It may be concluded that the coloration effect of pulsed laser on WO_3 is thermochromism.

Fig.5. SEM images of fresh (a), colored (b) and bleached (c) WO_3 samples

IV. CONCLUSION

Just by one pulse of laser irradiation, the color of WO_3 pellets turned to blue though a process different from ordinary photochromism, and the coloration may be attributed to thermochromism, and substoichiometric WO_{3-x} formed. For its stability and high efficiency, it is promising to be used in the field of information display or registration.

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