

Texture and Thermo-opto Nonlinearity of Composite TiO₂ and ZnS Thin Films

Qian Longsheng, Miao Tongqun, Wu Baoshen,

Ye Xiangyun, Ren Bing, Jin Tianfeng, Zhu Xiufang, Li Xiuyu
and Yuan Youxin

Abstract

Some works have been done on composed TiO₂ and ZnS thin films made from mixed materials. In the case of composed TiO₂ thin films, it is found that the metallic oxides with three or five valences could enhance the textural stability of TiO₂ thin film. By studying on composed ZnS thin film, we improved its nonlinear thermal refractivity.

Key Words: Mixed Material, Textural Stability, Nonlinear Thermal Refractivity

1. Introduction

TiO₂ and ZnS thin film are the charming optical coating for some special application, respectively. In order to improve their characteristics, we chose a much cheaper and easier way, which is to compose other proper substance in the films, by evaporating mixed materials using common EB device.

This paper describes our recent works on enhancing the textural stability of TiO₂ thin film and thermorefractive nonlinearity of ZnS thin film. In our experiments, there was no crystallization occurring after baking 470°C for 4 hours in composite TiO₂ thin film, and the thermo-opto coefficient, $(1/n \cdot dn/dT)$, was up to $6.9 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ for composite ZnS thin film.

2. The Textural Stability of Doped TiO₂ Thin Film

1 Consideration

It is well known^[1,2], that TiO₂ thin film, deposited on the substrate with the temperature (T_s) lower than 300°C, is amorphous. On the electron diffraction pattern, there are only several blurred and widened diffraction rings, quite the same as that of showing by Fig. 7. As we know, amorphous is a substable state of texture. If it obtains enough energy for passing over barrier potential then its temperature raises to the critical value (T_c), the crystallization in the films occurs, including nucleation and the grain growth. Companying with more and larger crystals appearance,

the texture of the film transfers from amorphous to more stable state, such as polycrystal, while the diffraction rings become narrower and sharper. In our case, being heated at 430°C for 4 hours there are some bright spots on the diffraction rings corresponding to some of large treelike crystals among the polycrystal in the film, as showing by Fig. 1, photograph of diffraction pattern and appearance.



(x66,000 Times)

Fig.1 Appearance and diffraction of pure TiO₂ film with Ts 250°C, baked at 430°C for 4 hours. In it a lot of treelike grains and bright spots on the patterns transparency. Here, the textural stability of TiO₂, in thin film form, composed with Y₂O₃, Ta₂O₅ and Mo were investigated.

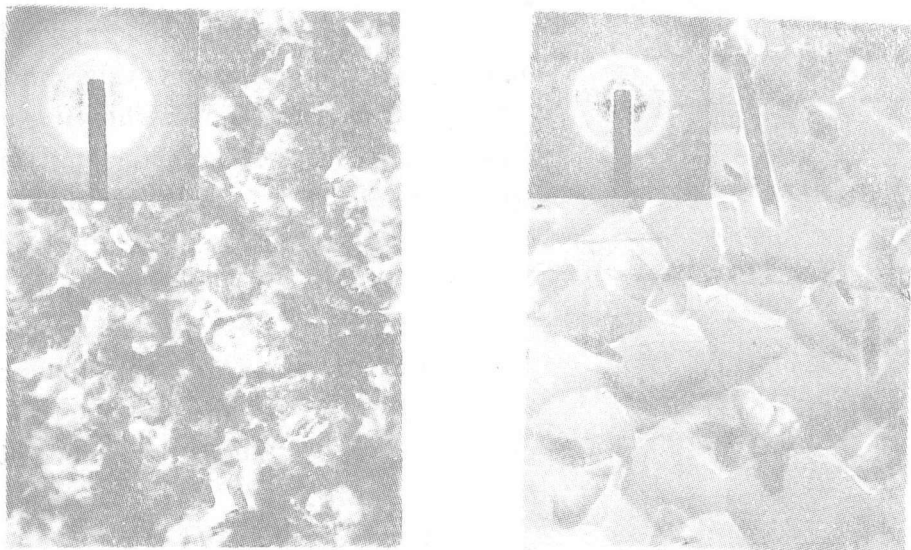
Generally, as our results mentioned above, the Tc of TiO₂ thin film is about 380°C - 400°C, which does not fit some special application, for example, high power laser technique. So, to enhance the Tc, or textural stability of TiO₂ coating is the interests of our studying.

M. Dorglas^[3] pointed out a phenomenon. When some oxides loss, bulk rutile TiO₂ is a semiconductor and have some optical absorption. However, the metallic ions with three- or five-valence could combine the suboxide Titanic to make the rutile bulk into insulator and optical transparency.

2. Experiments and Results

By evaporating various composite materials in weight proportion of 2:1, 3:1, 4:1 for TiO₂: Ta₂O₅, 10:1 for TiO₂: Y₂O₃, 6:2:2 for TiO₂: Ta₂O₅: Y₂O₃ and 10:1:0.5 for TiO₂: Y₂O₃: Mo, the films were deposited on the substrate with the various Ts about room 150°C and 250°C, by EBA-6DA with e-beam gun made in Japan. Then after being heated at the temperature of 430°C, 450°C and 470°C for 4 hours, respectively, the appearance and electron diffraction patterns of every kind of samples were observed under TEM in order to get the information about texture. Fig. 2, 3, 4, 5, 6 and 7 are the photographs taken in the experiments. From them something can be seen very interesting. For the films from same starting materials of TiO₂: Ta₂O₅ in every proportions and TiO₂: Y₂O₃ the higher Ts the films deposited on, the more stable the texture is. There are Fig. 2-a, b and Fig. 4-a, b corresponding to the samples from TiO₂: Ta₂O₅ in 2:1 and 4:1 respectively, both to show the same things, even though at different baking temperature. After baking, there are more and larger crystalline

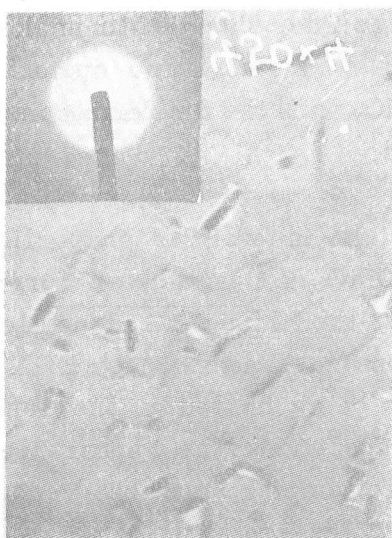
grains in the film with the lower T_s than that of the samples with 250°C . Both from appearance or diffraction patterns, shown by Fig. 2-a, b and 4-a, b respectively, it could be seen obviously.



(a) x66, 000 Times

(b) x66, 000 Times

Fig. 2 Appearance and diffraction of the films from 2:1 baked at 470°C with T_s of room a), and 250°C b). In a), more and larger grains with clearer and sharper rings than those in b)

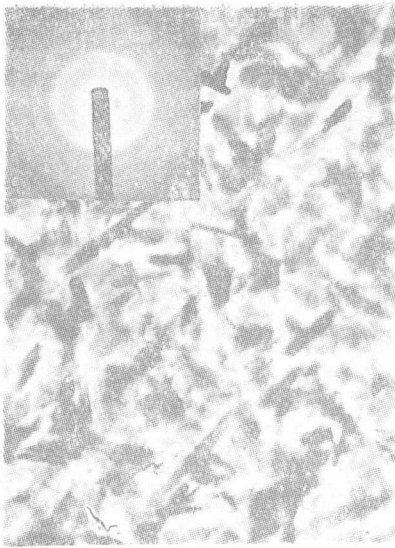


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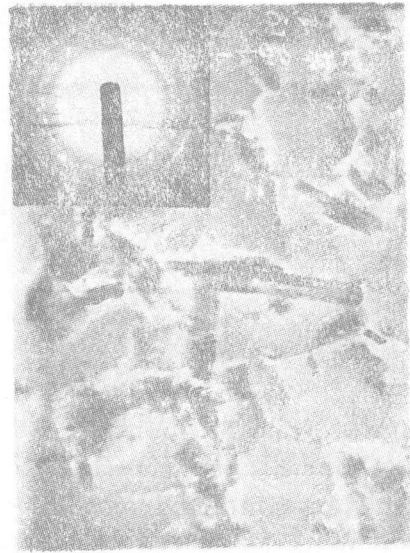
Fig. 3 For the film from 3:1 baked at 450°C with T_s of 250°C . Crystallization just occurred in the film with some spots on the patterns

The second thing can be seen here, is that for the samples from every proportions of $\text{TiO}_2:\text{Ta}_2\text{O}_5$ with the same T_s . Simplifying, only that of the samples with the T_s of 250°C are given here. After baking at 450°C , there is no change in the film from 2:1, which is not shown here because it can be referred by Fig. 7, as in the film from 3:1, the crystallization just occurred, and in the mean while, the crystalline grains have grown much larger for the films from 4:1. It can be seen from both the appearances and diffraction patterns in Fig. 3 and 4-b). Of course, for the same sample but baked at different temperature, the higher temperature

baked at, the more and larger crystalline grains appear in the film, Fig. 5-a, b, from $\text{TiO}_2, \text{Y}_2\text{O}_3$ with the T_s of 250°C , give us the example. In Fig.



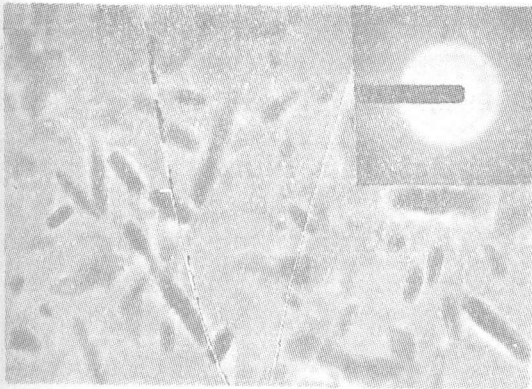
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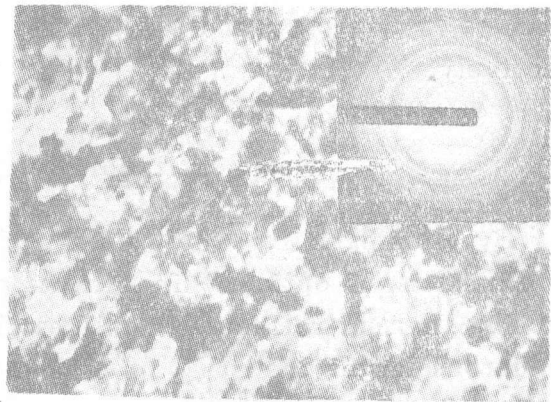
(b) x66,000 Times

Fig. 4 For the film from 4: 1 baked at 450°C with Ts of 180°C a) , and 250°C A lot of crystalline grains distribute homogeneously with clearer and sharper rings in a) . In b) , the few grains in the films but a lot of small bright spots on the patterns

5-a, a familiar graph can be seen after baking at 450°C, some grains in the film and more or less bright spots on the patterns. But after baking at 470°C, so many grains in the film that the diffraction pattern is almost the one of polycrystal.

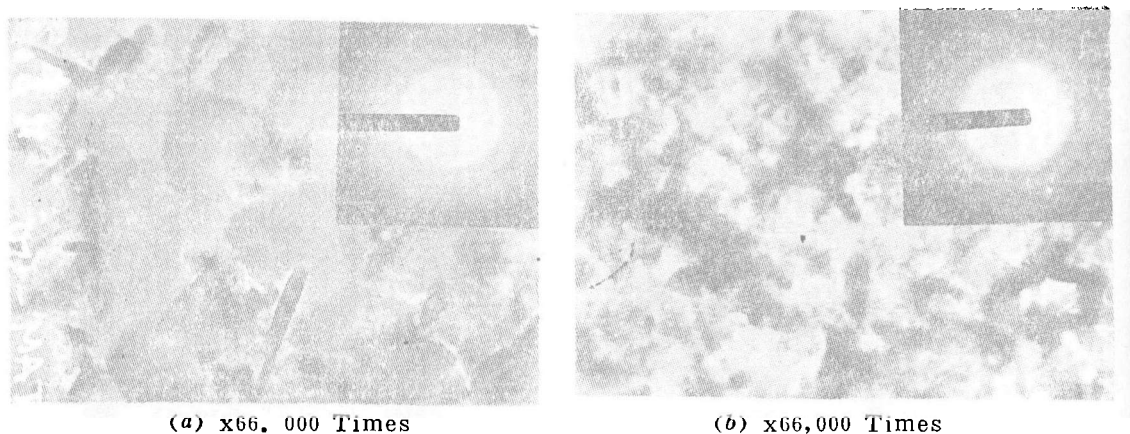


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Fig. 5 For the films from $TiO_2:Y_2O_3$ in 10: 1 with the Ts of 250°C baked at 450°C a) , and 470°C b) . Some bar grains is in the film with some spots on the pattern, from a) . By b) , numerous grains in the film and almost pattern of polycrystal in diffraction



(a) x66,000 Times

(b) x66,000 Times

Fig. 6 From $\text{TiO}_2: \text{Y}_2\text{O}_3: \text{Mo}$ after baking at 430°C , a) the film with Ts of 250°C , and b) the one with Ts of room

For the samples from $\text{TiO}_2: \text{Y}_2\text{O}_3: \text{Mo}$, the things are quite different, as shown by Fig. 6-a, b. After baking at 430°C , crystalline grains in the film with the Ts of 250°C are much more than that of room. On diffraction patterns, it can be seen there are a lot of bright spots for Ts of 250°C . That means the texture of the film with Ts of 250°C is less stable than that of room.

Nevertheless, for the film from $\text{TiO}_2: \text{Ta}_2\text{O}_5: \text{Y}_2\text{O}_3$ in 6:2:2 with the Ts of 250°C , remains its amorphous texture after baking at 470°C for 4 hours. Fig. 7, the appearance and diffraction pattern, shows it very clearly.

In our experiments, the amount of Ta_2O_5 in the composite films with the Ts of 250°C , which were determined by technique of emission spectrography (AES) and plasma spectroscopy of mode JY-38 made in France, were 16.75%, 11.14% and 6.28% for those from 2:1, 3:1 and 4:1, respectively.

3. Nonlinearity of Composed ZnS Thin Films

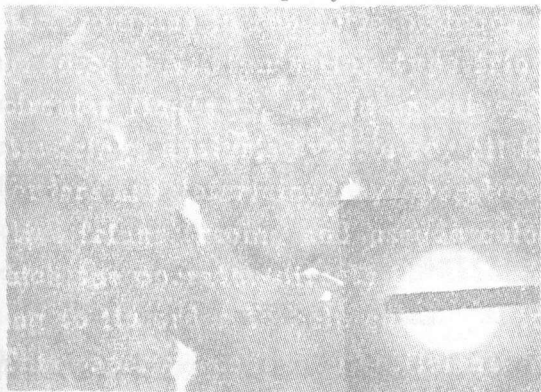
By summarizing the works of other authors^[4,5] on dealing with nonlinearity of optical thin film, it can be seen, generally, that the refractive thermal-refractive nonlinearity of the evaporated thin films is numerous larger than that of bulk materials, because of their microcrystalline structure as well as nonstoichiometric composition and defection to make the band edge of absorption decline toward long-wave region. In recent years, nonlinear elements in thin film form, especially applied in optoelectronics, received more and more attention all over the world. It is the ZnS that is one of the most interesting materials. However, for ordinary evaporated ZnS thin film, its thermo-refractive coefficient

is about $4 - 5 \times 10^{-4}/^{\circ}\text{C}$, and the film has poor antimoisture ability. Obviously, these properties would not satisfy the requirement in practical application on opto-electronics.

Also, by means of composing other proper materials, we have improved them. The consideration on selecting materials was based on two concepts, which the composed material might be favorite to enhance the thermal nonlinearity as well as to improve the microstructure. In our case, little amount of Cu and ZnSe were accepted because of its nonlinearity and some good mechanics. By evaporating ZnS, ZnSe and Cu mixture as coating material, composed ZnS thin film was made. Dramatically, the film has the very fine and homogeneous microstructure, shown by Fig. 8-a, comparing with that of ordinary columnar one, which is rough and inhomogeneous, as Fig. 8-b shows. Then it was baked at 300°C for 2 hours. Comparing the appearance and electron diffraction of the film before and after baking, showing as Fig. 9-a, b, it can be found that the textures were some different, that, after baking texture of the film changed into much better polycrystal, Fig. 9-b. with the sulphide of 97% in stoichiometry determined by the methods mentioned above, the film has the thermo-opto coefficient $(1/n) * (dn/dT)$ of $6.9 \times 10^{-4}/^{\circ}\text{C}$. It is much larger than that of ordinary one, about $4 - 5 \times 10^{-4}/^{\circ}\text{C}$.

4. Conclusion

Summarizing our experiments on composite TiO_2 and ZnS thin film, it can be seen very significantly, that some properties of the film might be changed by composing proper materials. In the case of composed TiO_2 thin films, the effect of the metallic ions with three or five valence on the texture of TiO_2 layer is obvious, which could enhance the critical



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Fig. 7 For the film from 2:1 with 250°C after baked at 470°C for 4 hours. It maintains its ordinary amorphous texture

temperature above 470°C , much higher than that of ordinary one, about 400°C . For composed ZnS film, its thermo-opto nonlinearity was also enhanced up to $6.9 \times 10^{-4}/^{\circ}\text{C}$, but the regular one has not been found, yet. It is worth pointing out, the results given here are not optimum ones, it seems to us.

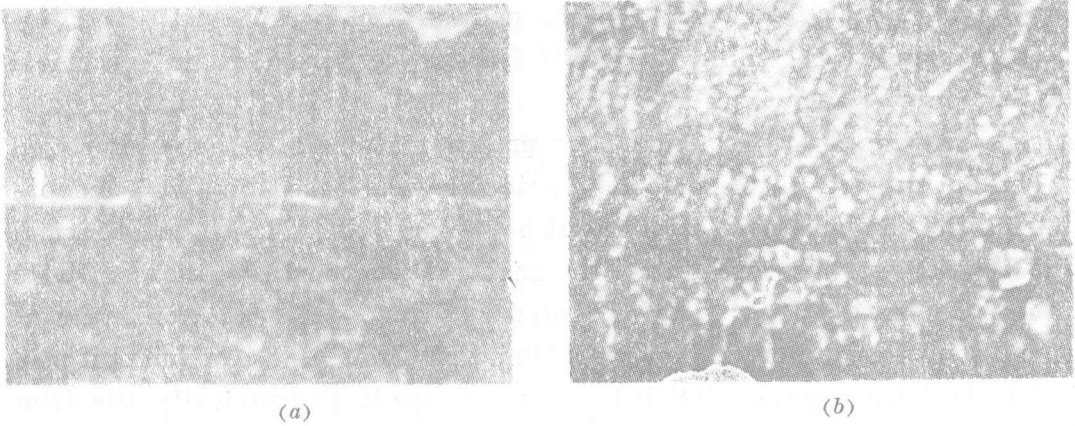


Fig. 8 Appearances of the composite ZnS film a) ,and ordinary one b) . In a) , the microstructure is very fine and homogeneous, comparing with obvious columnar and roughness in b)

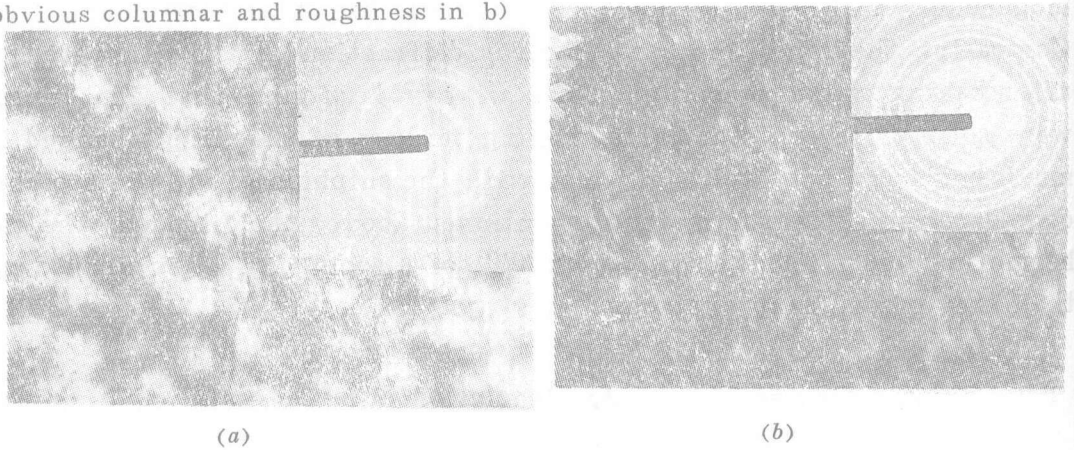


Fig. 9 Appearance and electron diffraction of the composite ZnS thin films before, a) and after, b) baking. From b) , the texture of baked film is better polycrystal than that of a)

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TiO₂和ZnS混合膜的结构和热光非线性性质

钱龙生 缪同群 吴宝申 叶祥云 任 兵 金天峰 朱秀芳 李秀玉 袁幼心

摘要: 对用混合材料制备的掺杂 ZnS和TiO₂ 薄膜的研究方面做了些工作, 发现 3 价或 5 价的金属氧化物能提高TiO₂薄膜结构的稳定性、通过对 ZnS 掺杂薄膜的研究, 我们提高了它的非线性热光系数。

关键词: 掺杂薄膜; 结构稳定性; 非线性热光系数