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Array of PZT Films Preparation by Sol-gel Method

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The technique of fine patterning ferroelectric-films is the key technique of integrated ferroelectricity. In this paper, the novel technique had been developed to make fine patterns of 2D array of PZT films. At first, the photosensitive PZT gel films were prepared by sol-gel process with chemical modifier, then He-Cd UV laser was used to irradiate the gel films in different direction twice interference, the irradiated gel film was leached in organic solvent. At last, the 2D array of PZT films was obtained after heat treatment at 650℃ for 20min. At present, the 2D array of PZT films obtained with the method are about 0.9μm-1.4μm in periodic space, and node area and thickness of the array are (0.6μm-1.0μm)×(0.6μm -1.0μm) and 0.2μm -0.25μm respectively. The research is important in fabrication of micro-electric such as uncooled infrared detectors.

Key words: PZT film, Photosensitive, Sol-gel, Two dimension array

1. INTRODUCTION

Lead zirconate titanate (PZT) films have nice advantages in ferroelectricity, piezoelectricity, dielectricity and pyroelectricity, and have important application values in the fields such as ferroelectric random access memories(FERAM), uncooled infrared thermal imaging arrays, two dimension(2D) ultrasound arrays, etc.[1-7] In all of these applications, the ferroelctric films of apparatus need to be patternized, and the structure and size of fine patterning ferroelectric-films decide the integrated level and quality of apparatus. So the technique of fine patterning ferroelectric-films is the key technique of integrated ferroelectrics. The fine patterning in common are chemical etching, reactive ion etching or chemically assisted ion-beam etching, these fine patterning processes are complex in process and difficult to obtain regular and fine patterns in many cases.

The author of this paper has used the chemical modification method to prepare the photosensitive gel film of PZT, as well as the ultraviolet light processing method to obtain the fine patterns of the PZT film. Based on the same consideration, the pattern of grating or dot array of PZT films can be obtained using the He-Cd ultraviolet laser as light source to irradiate the gel films in different direction twice interference. And the crystal structure and ferroelectricity properties of films are further studied in this paper.

2. EXPERIMENT

To begin with, chemical modification agent benzoylacetone (BzAc) was mixed with methanol (MeOH) in terms of the molar ratio of 1:20 (labeled as BzAc/MeOH). And then, Zirconium oxynitrate ($ZrO(NO_3)_2 \cdot 2H_2O$) and tetrabutyl titanate ($Ti(O\text{-}nBu)_4$) were added to the above mentioned BzAc/MeOH solution in terms of the molar ratio of 1:20 individually, and after being stirred at the room temperature, two kinds of transparent and stable solutions such as sol containing Zr (labeled as Zr-sol) and sol containing Ti (labeled as Ti-sol) were obtained individually, lead acetate ($Pb(CH_3COO)_2 \cdot 3H_2O$) was added to the methanol in terms of the molar ratio of 1:20, and after being stirred at the room temperature, the sol containing Pb (labeled as Pb-sol) was obtained, in above processes, acetic acid (HAc) and ethanol amine (MEA) were added as addition agent, finally, three kinds of sols were mixed in terms of $Pb(Zr_{0.52}Ti_{0.48})O_3$ stoichiometric ratios, and were stirred in the hot bath at the temperature of 50℃ so as to obtain PZT sol. In order to compensate Pb missing and to inhibit the occurrence of pyrochlore phase due to the lack of Pb in heat treatment, when gel was prepared, Pb is 10% over the specified quantity. The PH value of the PZT sol was about 3-4.

The dip-coating technique was used to prepare the PZT films. ITO glass (7059 glass with ITO electric conduction layer), quartz glass and silicon chip were used as the substrates, ITO glass substrate was used in measuring characteristics of ferroelectricity and XRD. Quartz glass substrate was used in testing the ultraviolet-visible spectrum (UV spectrum) of PZT gel films. Silicon substrate is used in making fine patterns. The thickness of gel films prepared by using the dip-coating technique at the rate of 1mm/sec was about 0.3μm. After heat treatment, the thickness of PZT ceramic films was about 0.2μm.

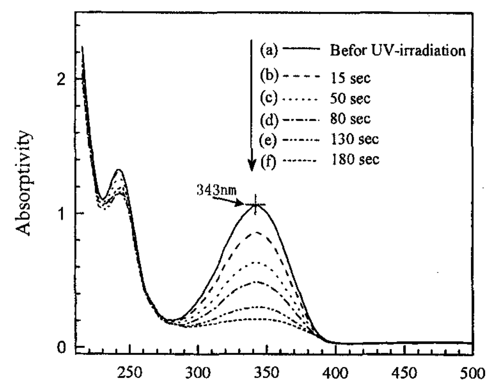
The PZT gel films are irradiated by the He-Cd ultraviolet laser as light source in once interference or in different direction twice interference. And then PZT gel films are leached in MeOH solution, the area irradiated by UV light remains completely, whereby obtaining PZT gel film interference patterns. After further heat treatment is made of them at the temperature of 680℃ for 30 minutes, fine patterns of PZT ceramic films with Perovskite structure are obtained.

As for gel films obtained from ITO glass substrate, ultraviolet Laser irradiation and the heat treatment was adopted under the same conditions mentioned above afterwards for carring out the tests of X-ray diffraction spectrum (XRD spectrum), and or golden (top) electrodes are sputtered over them so as to form the thin film electric capacitors for carrying out the tests of behaviors of ferroelectricity and dielectricity.

3. RESULTS AND DISCUSSION

3.1 Ultraviolet spectrum of PZT gel film

The ultraviolet spectrum of PZT gel films on the quartz substrate is shown in Fig.1(a), and its feature absorption peak appears near 343nm and between 336nm-360nm, where the absorption peak 360nm is just the absorption of $\pi \rightarrow \pi^*$ electronic transition of the chelates formed by Ti ion and BzAc,[10,12,13] and the absorption peak 336nm is just the absorption of the chelates formed by Zr ion and BzAc,[8] and the Pb ion cannot formed chelates with BzAc in Pb-sol in present research, so there is no effects on the absorption peak above mentioned,[4,14,15] whereby confirming that after the above sols were mixed, there was no variation in the basic structure of the chelates formed by Ti ,Zr ion and BzAc. This kind of chelate structure can stably exist in the gel films at the room temperature, whereby making gel films show the obvious ultraviolet photosensitivity.

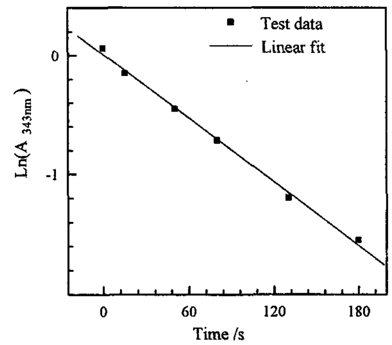


Fg.1 The ultraviolet spectrum absorption peak of PZT gel film and its intensity variation under the ultraviolet light irradiation

There is no obvious variation in absorption near 343nm as shown in Fig.1(a) in the process of drying PZT gel films at the temperature of 60℃, however, at the room temperature, when the He-Cd ultraviolet laser (325nm wavelength) is used to irradiate gel films, the absorption near 343nm obviously decreases as shown in Fig.2. Thus, illustrating that the chelates above mentioned are dissociated. The logarithm of the intensity absorption at around 343nm wave length (labeled as $Ln(A_{343})$) have the linear relationship with the irradiation time indicated in formula(1), which demonstrate that photodissociation process of the chelates belongs to first order reaction.[8-12]

$$Ln(A_{max})=0.075-0.0089\ T \tag{1}$$

With the dissociation of the chelates, the physical and chemical properties of gel films have the corresponding variations. It has been found via the experiments that ultraviolet laser irradiation can greatly reduce the solubility and soluble speed of gel films in such organic agents as ethanol, methanol and so on, and by using this characteristic, fine patterns of gel films can be obtained.



Fg.2 The relationship between intensity of absorption peak at 343nm of PZT gel film and the time of ultraviolet light irradiation

3.2 Two beam of ultraviolet laser interference patterning

The interference of two coherent beam of laser can be used to prepare grating for a long time, but the reports about the applications of microelectronic element are less. The main causes are the localization of one dimension period structure obtained by interference patterns is simple. Using multi-exposal and interference area overlap, we can obtain the complex structure of pattern, by which more fine one and two dimension pattern of PZT films in wider area than current optical etching method can be fabricated.

When two coherent light beam of He-Cd laser irradiate symmetrically in the PZT film plane, the ultraviolet light intensity distribution in the plane is illustrate as formula (2), the interference stripe period distance $d=\lambda/(2\sin\theta)$:

$$I = 2I_0(1+\cos(\frac{4\pi\sin\theta}{\lambda}x)) \tag{2}$$

I – the ultraviolet light intensity in interference field
I_0– the ultraviolet light intensity of one beam of He-Cd laser
λ – the light wave length of He-Cd laser
θ – the entrance angle θ

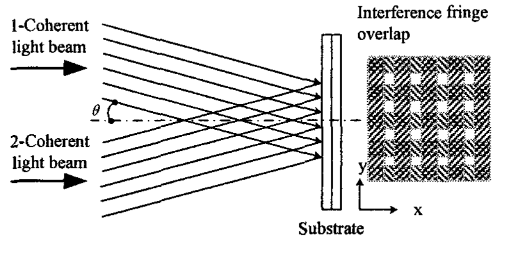


Fig.3 The interference fringe and their overlay of coherent light in interference field of substrate

The PZT films after once exposure carry out second exposure by rotated the film with 90°, the light intensity distribution in interference field illustrate as formula (3). The point array can be obtained from the cross node formed by *X*-axis and *Y*-axis direction, the period space in *X*-axis and *Y*-axis direction is d mentioned above. d can be shift along with the entrance angle θ, when the entrance angle θ in X-direction equal its Y-direction, the same period array square dot can be obtained, and otherwise the different period array oblong dot can be obtained. Using this method, the array dot thickness is confined by the coherent length of laser light as show in fig.3, so which fit to the pattern preparation of PZT films in bigger area. The schematic diagram of PZT film fine patterning as show in fig.4.

$$I = 2I_0(2+\cos(\frac{4\pi\sin\theta}{\lambda}x)+\cos(\frac{4\pi\sin\theta}{\lambda}y)) \quad (3)$$

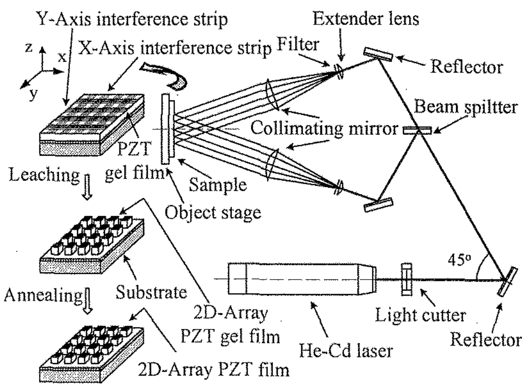


Fig.4 The schematic diagram of PZT film fine patterning by double interference exposure with two beam ultraviolet laser

3.3 2-Dimension array pattern of PZT films

In this research, PZT gel films were first prepared on the silicon substrate with film thickness of 0.3μm, and then He-Cd ultraviolet laser was used to irradiate the gel films in different direction (*X-Y*) twice interference with 5min in *X*-direction and *Y*-direction respectively at the room temperature and atmospheric conditions, the exposured gel film was leached in organic solvent methanol as the developing agent for 1-2 min. At last, the 2D dot array pattern of PZT films was obtained after heat treatment at 650℃ for 20min as show in Fig.5. The square lattice in light color is PZT films and the background part in dark color is substrate. The array is about 1.4μm in periodic space, and node area and thickness of array are 1.0μm×1.0μm and about 0.2μm respectively .

Prolonging the irradiation time from 5min in *X*-direction and *Y*-direction to 6min respectively, after developing and heat treatment procedure above mentioned, the combinative pattern structure of dot array and lattice of PZT film can be obtained as shown in fig.6. The grid and dot in light color is PZT films and the background part in dark color is substrate. The array is about 0.9μm in periodic space, and node area and thickness of array are 0.6μm×0.6μm and about 0.25μm respectively .

Further prolonging the irradiation time from 6min in *X*-direction and *Y*-direction to 10min respectively, after developing and heat treatment procedure above mentioned, the lattice structure pattern of PZT film can be obtained as shown in fig.7. The grid and node in light color is PZT films and the background part in dark color is substrate. The lattice is about 0.9μm in periodic space, and node area and thickness of array are 0.6μm×0.6μm and about 0.2μm respectively .

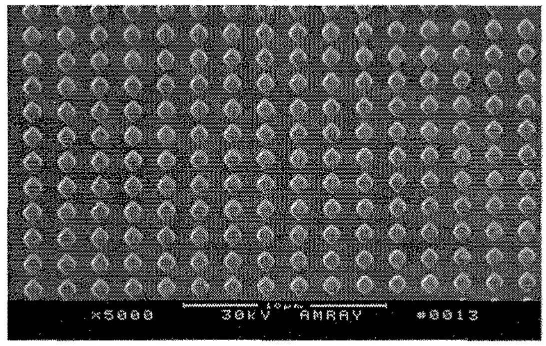


Fig.5 SEM photo of the dot array structure pattern of PZT film

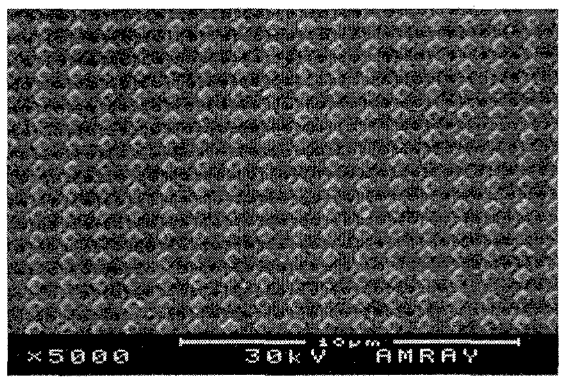


Fig.6 SEM photo the combinative structure pattern with dot array and lattice of PZT film

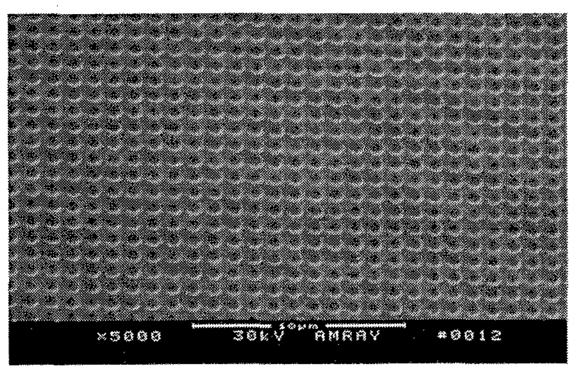


Fig.7 SEM photo of the lattice structure pattern of PZT film

3.4 Crystal structures and ferroelectricity of the PZT film

PZT gel films on the ITO glass substrate were prepared adopting dip-coating method, irradiated by ultraviolet light for 3-4min, dried in the baking box with the temperature at 250℃ for 15 min, and then, annealed in resistance furnace with the temperature at 680℃ for 30 min. And at last, PZT ceramic films were obtained, XRD diffraction patterns of the PZT films prepared by this method is shown in fig.8, which indicate that the PZT ceramic films is of typical perovskite structure, and hysteresis loop is also shown in fig.9 via Sawyer-Tower circuit at a frequency of 50Hz and an applied voltage of 5V, and the remanent polarization Pr=12μC/cm^2, and the coercive field Ec=25kV/cm.

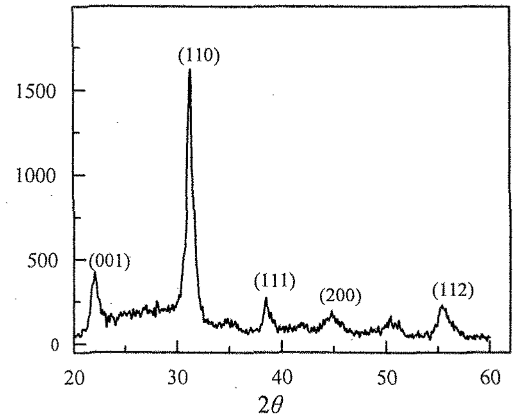


Fig.8 XRD diffraction patterns of the PZT films

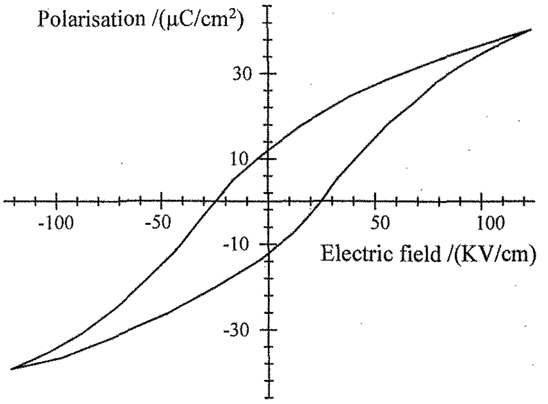


Fig.9 The curve of hysteresis loop of PZT film

4. CONCLUSIONS

The photosensitivity of PZT gel films have been prepared using chemical modification combining with sol-gel technique. The novel technique of making fine 2D array pattern of PZT films via twice-interference of two light beam of ultraviolet laser has been developed. After the further heat treatment, the 2D array of PZT films obtained with the method are about 0.9μm-1.4μm in periodic space, and node area and thickness of array are (0.6μm-1.0μm)×(0.6μm-1.0μm) and 0.2-0.25μm respectively.

The optical system for fine patterning by Interference overlap is simple, and not requiring the mask or complex curved optical elements. the method can give wider interference field, and the fine periodic space about λ/2.

Combining with traditional photoetching, this technique is helpful to prepare the period structure pattern in sub-micron for micro-electronic element and photoelectronic device such as DRAM cell, infrared detector array and so on.

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REFERENCES

[1] R. W. Whatmore, Q. Zhang, Z. Huang, et al., Materials Science in Semiconductor Processing 5, 65-76 (2003).
[2] A. Z. Simoes, A. H. M. Gonzalez, M. Cilense, M. A. Zaghete, B. D. Stojanovic, J. A. Varela, Ceramics International 28, 271-277 (2002).
[3] M. Es-Souni, M. Abed, A. piorra, S. Malinowski, V. Zaporojtchenko, Thin Solid films, 389, 99-107 (2001).
[4] Q. Zou, S. Nourbakhsh, J. Kim, Materials Letters 40, 240-245 (1999).
[5] J. A. Ruffner, P. G. Clem, B. A. Tuttle, C. J. Brinker, C. S. Sriram, J. A. Bullington, Thin Solid films, 332, 356-361 (1998).
[6] Aiying Wu, Li Yang, P. M. Vilarinho, I. M. Miranda Salvado, J. L. Baptista, Journal of European Ceramic Society 17, 1443-1452 (1997).
[7] WeiGuo Liu, Jong Soo Ko, Weiguang Zhu, Thin Solid Films 371 254-258 (2000).
[8] Bernd Matthes, Gerhard Tomandl, Gunter Werner, J. European Ceramic Society, 19, 1387-1389 (1999).
[9] Jong-Kuk Kim, Nam-Kyoung Kim, Byung-Ok Park, Materials Letters 39, 280-286 (1999).
[10] N.Tohge, G.Zhao, F.Chiba, Thin Solid Films 351 85-90 (1999).
[11] GaoYang Zhao, Noboru Tohge, Materials Research Bulletin, 33(1), 21-30 (1998).
[12] Z. Weihua, Z. Gaoyang, C. Zhiming, Materials Science and Engineering B, 99, 168-172 (2003).
[13] K.Simmons-Potter, B.G.Potter Jr., D.C.Meister, et al., Journal of Non-Crystalline Solids 239, 96-103 (1998).
[14] Naoshi Ozawa, Takeshi Yao, Solid State Ionics, 151, 79-87 (2002).
[15] Kintaka Kenji, nishii Junji, Tohgr Noboru, The International Society for Optical Engineering, 3943, 38-46 (2000).

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