X ray photoelectron spectroscopy (XPS) analysis of Photosensitive ZrO2 array

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Abstract. Based on organic zirconium source as the starting material, by adding chemical modifiers which are made up with photosensitive ZrO2 sol. A uniformed ZrO2 array dot was fabricated with a mean diameter of around 800 nm. By using UV-vis spectra and X-ray photoelectron spectroscopy analysis method, studies the photosensitive ZrO2 gel film of photochemical reaction process and the photosensitive mechanism, to determine the zirconium atom centered chelate structure, reaction formed by metal chelate Zr atom for the center, and to establish the molecular model of the chelate. And studied the ultraviolet light in the process of the variation of the XPS spectra, Zr3d 5/2 to 184.9 eV corresponding to the binding energy of the Zr=O=C; Zr=O=C as the combination of state peak gradually reduce; By combining with the status of Zr-O peak gradually increase; The strength of the C=O peak is gradually decline. This suggests that in the process of ultraviolet light photochemical reaction happened. This study is of great significance to the micro fabrication of ZrO2 array not only to the memory devices but also to the optical devices.

1. Introduction

Resistance switching memory (RRAM) because of its fast response, high stability, low power consumption is expected to become a new generation of memory, the development and application of this type of memory involves a lot of problems, including micro-fabrications process. As for the ZrO2 thin film, it is also widely used for Optical-electronic devices which are depended on the development of micro-fabrications technology, from the integrated circuit to the integrated optics, learned from the microelectronics and micro-optics. Thin film materials species also have more compounds, such as semiconductor, metal type, all kinds of materials can be suitable for different uses. Such as the oxide Al2O3, Bi2O3 and Sb2O3, Nd2O3, ZrO2, TiO2 and SiO2, PbO, etc; Semiconductor Si, Ge, etc; And metal materials Au, Ag, Al, Cu, Cr, etc. Zirconium oxide film with its high melting point, low thermal conductivity, high ion conductivity and high chemical stability, widely used in the preparation of high performance structure ceramics. And also zirconium oxide film has good optical properties, such as high refractive index, low absorption rate and high dielectric constant, making it in optical wave guide
devices, metal oxide field-effect tube device, ferro-electric memory medium.

Prof. Zhao’s group applied to such as thin film with photosensitive chemical modification method, can be carried out on the thin film micro fabrication. In this paper, through sol-gel method combined with ultraviolet photographic process, the preparation of the ZrO$_2$ array. By using UV-vis spectra and X-ray photoelectron spectroscopy analysis method, studies the photosensitive ZrO$_2$ gel film of photochemical reaction process and the photosensitive mechanism.

2. Experimental

Based on the Butanol zirconium (Zr(OC$_4$H$_9$)$_4$) as the starting material, adding benzoyl acetone (BzAcH) is a chemical modifier (mole ratio of 1: 0.78). (CH$_3$CH$_2$OH) anhydrous ethanol as a solvent, the preparation of ZrO$_2$ photosensitive sol. Adopt pulling method respectively in quartz board and silica gel film substrate preparation. Quartz plates used for the determination of ultraviolet spectrum. Silicon substrates used in the study of array micro machining and XPS spectrum. Use laser wavelength of 325 nm He - Cd (Kimmon Electric, total power of 50 mW) emits a stable light source, with similar to the results of the beam is decomposed into energy into two beams of coherent beam. The optical beam path diagram settings as shown in figure 1 [8]. Two beams of light interference pattern after the intervention. The interference pattern after 0 to 120 seconds of photosensitive photosensitive, again after soluble in anhydrous ethanol to wash, ZrO$_2$ array can be obtained. The preparation of array with double beams, two exposure laser interferometry. The AFM morphology is shown in figure 2. Figure 2 (1) for the plan of the array, figure 2 (2) for 3 d graphics array, the array lattice size is the same, which is about 800 nm.

By using UV-vis spectra and X-ray photoelectron spectrum analysis method, studies the ZrO$_2$ photosensitive film photochemical reaction process and the photosensitive mechanism. Test using British KRATOS AXIS type ULTRA X ray photoelectron spectrometer for ZrO$_2$ photosensitive film analysis of chemical composition and elemental chemical state; USES the Japanese electronic SII ZrO$_2$ array with atomic force microscope surface morphology observation. Use the Japanese Jasco UV- vis ultraviolet spectrophotometer of ZrO$_2$ photographic film to determine the ultraviolet spectrum.

![Figure 1](image_url)  
*Figure 1. Optical paths for photosensitive process diagram*
3. Results and discussions:

3.1. Ultraviolet spectrum analysis of ZrO$_2$ photographic film

Using the wavelength of 325 nm uv laser film, film of ultraviolet absorption spectrum variations over time as shown in figure 3, with the extension of irradiation time, the gel film of chelate structure constantly is broken down, the corresponding characterization of chelate content of characteristic absorption peak height decreases gradually. Gel membrane absorption peak near 335 nm in basic disappearance, chelate has been largely after decomposition.

![Figure 3](image3.png)

**Figure 3.** UV-vis spectra curves of ZrO$_2$ array with different exposure time of UV light.
3.2. Ultraviolet laser exposure in the process of X-ray photoelectron spectroscopy (XPS) analysis

X-ray photoelectron spectroscopy analysis that is, not only to do qualitative analysis, through wide spectrum analysis to determine ZrO$_2$ photographic film is contained in elements; But also can do the analysis of the chemical state through high resolution spectrum analysis to determine the chemical state of element. First gel film XPS analysis, in the absence of uv light energy acquisition wide spectrum range is 1100 ~ 0 eV, step 1 eV, adopts the Al K$_\alpha$ as the incident light, the energy of 1486.6 eV. The binding energy of the calibration using C1s (284.8 eV). By ZrO$_2$ gel film photoelectron spectroscopy diagram in figure 4, the study found the chemical elements contained in the gel film for Zr, C, O, the elements of the photoelectron peak as shown in figure 4.

Because Zr3d level of multiplet split, split into Zr3d$_{5/2}$ and Zr3d$_{3/2}$. As shown in figure 4 - (2), Zr3d$_{5/2}$ is 184.9 eV, Zr3d$_{3/2}$ to 186.5 eV. The Zr3d$_{5/2}$ to 184.9 eV corresponding Zr-O-C binding energy of the binding energy than Zr-O shift towards high binding energy of 1.5 eV, which shows that the gel film formed as shown in the chelate in formula (1).

As shown in figure 5, in the absence of UV laser exposure, C1s XPS spectra of four chemical state, after to Gauss fitting diagram C1s, found four chemical state of C1s, of which the chemical state of C=O 286.6 eV is stronger. A chemical state of 284.8 eV C1s, which is the chemical state of C-H combination; two other chemical state were 288.1 eV and 289.9 eV C1s, which are C with C=O bond and C=C respectively. This shows that the absence of UV laser exposure, C atoms mainly C=O combination, forming gel film, such as chelate in formula (1).
In order to study the photochemical reaction occurred in the process of UV irradiation, we undertook different UV laser exposure time of ZrO2 gel film XPS analyses. Zr3d and C1s of XPS high resolution spectra with different UV laser exposure time varied. Significantly difference happened before and after UV laser exposure, and that with the increase of exposure time, Zr3d and C 1s spectrum are changing, too.

Of the energy level splitting Zr3d Zr3d5/2 and Zr3d3/2, figure 5 is UV irradiation Zr3d photoelectron energy spectrum diagram of 20 seconds. Diagram you can see the XPS Zr3d map, there are two kinds of chemical state after Zr3d for Gauss fitting in the figure, find a chemical state Zr3d5/2 is 184.9 eV, Zr3d3/2 is 186.5 eV, a chemical state with Zr-O=C combination; Another state chemical Zr3d5/2 is 182.5 eV, Zr3d3/2 is 184.0 eV, it is combined with Zr-O state. Compared with figure 2 without UV irradiation, appeared Zr3d5/2 peak of 182.5 eV, and Zr3d5/2 is 184.9 eV peak position has not changed, the strength of the peak of 184.9 eV has a downward trend, suggesting that photochemical reaction happened after UV irradiation, the peak position of Zr3d5/2 (184.9 eV) peak in the gradual decomposition, and (2) happened such as type shown in photochemical reactions.

UV irradiation exposure time of 80 seconds, as shown in figure 6, Zr3d photoelectron energy spectrum diagram, Zr3d5/2 compared to the peak of 184.9 eV has disappeared, only a chemical state Zr3d5/2 is 182.5 eV's peak, Zr3d5/2 is 182.5 eV chemical state to Zr-O bond, namely formula (2) of the material after reaction. This shows that in 80 seconds after UV laser irradiation, Zr chelate has been completely decomposed into Zr-O state, chelation of gel films have broken down completely.

\[
\text{(C}_4\text{H}_9\text{O})_2\text{Zr} + \text{CH}_3\text{C} = \text{C} - \text{CH}_2 - \text{C} = \text{C}_6\text{H}_5 \quad \text{UV light} \quad \rightarrow \quad \text{(C}_4\text{H}_6\text{O})_2\text{Zr} + \text{CH}_3\text{C} = \text{C} - \text{CH}_2 - \text{C} = \text{C}_6\text{H}_5
\]

As the growth of the UV irradiation exposure time, ultraviolet laser when 20 seconds of C 1s photoelectron energy spectrum diagram as shown in figure 5, chemical state of C1s are mainly two kinds of 286.6 eV and 284.8 eV. In figure 5 no ultraviolet spectrum, chemical state is 286.6 eV C1s peak on the decline, chemical state is 284.8 eV C1s peak rising, suggesting that after UV laser exposure, C elements combined with state from C=O to C-H. It also suggests that, after UV laser irradiation, gel film happened such as formula (2) as shown in the reaction.
When the UV irradiation exposure time of 80 seconds of C1s photo electron energy spectrum diagram as shown in figure 6, four chemical state of 284.8 eV C1s peak intensity, the largest chemical state of the C1s peak of 286.6 eV figure 4-6 down a lot of strength, C atom is based on the C of C-H. Compared with figure 4 to 8, it also suggests that gel films after uv irradiation in 80 seconds of photo chemical reaction is complete. The curves showed that with the increase of illumination time, the combination of the C1s state from which focuses on the C≡O to C-H is given priority to, this suggests that with the ultraviolet irradiation, gel film photo chemical reaction happened.

4. Conclusion
Based on organic zirconium source as the starting material, by adding chemical modifiers made up with photosensitive ZrO2 sol. A uniformed ZrO2 array dot was fabricated with a mean diameter of around 800 nm. By using UV-vis spectra and X-ray photo electron spectroscopy analysis method, studies the photosensitive ZrO2 gel film of photo chemical reaction process and the photosensitive mechanism, UV - Vis and XPS spectra analysis to determine the zirconium atom centered chelate structure, reaction formed by metal chelate Zr atom for the center, and to establish the molecular model of the chelate. And studied the ultraviolet light in the process of the variation of the XPS spectra, Zr3d5/2 to 184.9 eV corresponding to the binding energy of the Zr\equiv O \equiv C; Zr\equiv O \equiv C as the combination of state peak gradually reduce; By combining with the status of Zr-O peak gradually increase; The strength of the C≡O peak is gradually decline. This suggests that in the process of ultraviolet light photo chemical reaction happened. This study is of great significance to the micro-fabrication of ZrO2 array.

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