

A Versatile Method for Preparing Metal Oxide Nanostructures via Laser Direct Patterning

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Abstract

Amorphous metal-oxides have emerged as potential replacements for organic and silicon materials in thin-film electronics. In past few years, many approaches have been proposed to direct-pattern metal oxide nanostructures. However, one main limitation was the low applicability of synthesis approaches to different material. To overcome this challenge, a versatile route for preparing photosensitive metal oxide precursor is proposed. We show that pure or mixture of metal oxide nanostructures can be obtained with suitable electronic properties for microelectronic applications.

1. Introduction

Nowadays, photopatternable metal oxide precursors have attracted a great deal of attention in nanotechnology due to their high interest in low cost and non-vacuum fabrication process. Several works have been presented and shown their abilities to direct-pattern metal oxide structures in submicro or nanoscale dimensions by Deep Ultra-Violet (DUV) lithography, Extreme Ultra-Violet (EUV) lithography, and Electron-beam (e-beam) lithography [1-4]. However, the mechanism of photoreaction is different from one to the others depending on the preparation method of metal oxide precursor. This difference limits the possibility of the technique itself to be widely apply in semiconductor industry. Therefore, a universal method for preparing photosensitive metal oxide resist is needed.

The aim of this work is to demonstrate a concept of general preparation of photosensitive metal oxide clusters (MOCs) for micro- and nanofabrication. The oxo-cluster was further formed by a partial hydrolysis of metal alkoxide, such as Zn, Ti, Zr, Hf, controlled by complexation by methacrylic acid. These molecular building blocks are designed to absorb certain incident energy, enabling the direct photopatterning process. In the present case, MOCs were design to be sensitive to DUV light (193 nm). Thanks to the nanosize of the building blocks, homogeneous patterns and high-resolution lithography can be realized. Moreover, the versatility of these method is not limited to only few metal alkoxides. By doping with other ions, mixed metal oxide like InGaZnO, TiInO or Co:ZnO can be obtained.

2. Result and discussion

Metal oxo-cluster preparation and photoreaction mechanism

Fig. 1 shows a schematic diagram of MOCs preparation and the crosslinking process induced by photocleavage reaction. In the first step, metal alkoxide precursors $M(OR)_x$, $M = Zn, Ti, Zr, Hf$, are mixed with excess amount of methacrylic acid (MAA) to favor the exchange of organic ligand. MAA ligands act as stabilizers to limit the condensation reactions then preventing precipitation, enabling the formation of homogeneous film during spin-coating process. The bonding between metal core and MAA ligand can be cleaved by receiving an energy higher than the bonding energy [5]. After cleavage of the bonding, crosslinking process of MOCs no longer protected by MAA can occur. As a result, the oxo-bridge can be from among metal core, thus achieving metal oxide network. The crosslinked metal oxide network is insoluble in developer, making it possible to direct pattern metal oxide by laser lithography.

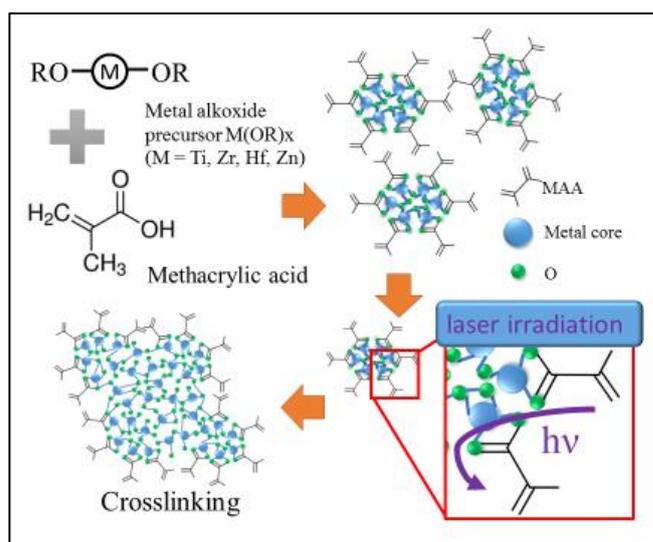


Fig. 1 Schematic representation of the precursor preparation and the photo crosslinking mechanism.

Study of photocrosslinking reaction by FTIR

To confirm the photocrosslinking reaction mechanism,

among other analysis techniques, FTIR analysis was performed on two different MOCs, based on Zinc (ZnOC) and Titanium (TiOC). Fig. 2a) and b) show the evolution of FTIR spectrum of ZnOC and TiOC thin film irradiated with DUV lamp (broad emission band from 200 to 350 nm) for 600 s. As shown in Fig. 2a), a gradual decrease of bands at 1573 and 1417 cm^{-1} were observed. These two bands are referred respectively to the asymmetric and symmetric stretching of COO^- group complexed with metal core [6]. Thus, a small shift of these two bands, 1552 and 1430 cm^{-1} , is observed in Fig. 2b) due to the electron affinity of different metal core. In contrary, an increase of the band located at 1730 cm^{-1} can be noticed in both spectrum, which corresponds to free COO^- groups. The results above indicate that during the DUV irradiation the metal-MAA bonds were cleaved, and free MAA was released from the complex, provoking the crosslinking process of metal oxide metal(M-O-M) network.

To evaluate the potential of the MOC solution as a negative tone resist, the film was exposed to a laser interference pattern by a homemade optical system. Top view AFM images and cross-section profiles of both material are shown in Fig. c), d). The period of pattern is 600 nm and the thickness of 70 nm could be achieved. No distortion and residue between lines was observed in each resist. Moreover, no significant difference could be found between both MOC resist. This result show a nice versatility and an excellent photopatterning ability of our MOC solution. Similar results could be obtained with MOC solution from Zr or Hf precursors.

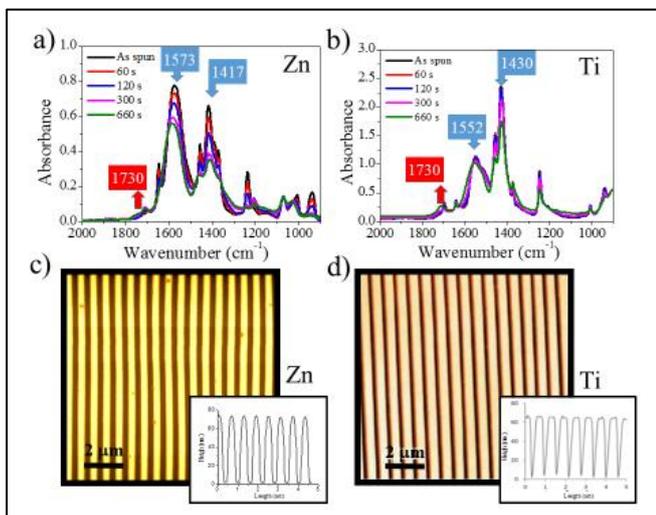


Fig. 2 FTIR analysis of photo reaction by exposure to DUV light and AFM image showing the photopatterning of Zinc a), c) and Titanium b), d) metal oxide precursors.

Doping effect on transistor characteristic

To demonstrate the high applicability of this MOCs resist and the interest of mixture of metal oxide, we used ZnOC as a matrix and doped it with Indium(III) nitrate hydrate (99.99% Sigma Aldrich) and Gallium(III) nitrate hydrate (99.99% Sigma Aldrich). The molar ratio of In:Ga:Zn was fixed as 4:1:2. Thin film transistors with different MOCs as active layer were made to compare transistor characteristics.

The prepared solutions were spin-coated on a heavily doped p-type Si wafer with a 100-nm-thick silicon nitride (Si_3N_4) layer that served as gate electrode and gate dielectric. In the case of pure ZnOC, the spin coated thin films were patterned by DUV irradiation and then annealed at several temperatures from 300 $^{\circ}\text{C}$ to 600 $^{\circ}\text{C}$ in air for one hour. In the end, Al electrodes were deposited on the top to measure electrical properties. Their transfer characteristics are shown in Fig 3a). The ZnO TFT annealing at 300 $^{\circ}\text{C}$ shows no semiconducting behavior. From 400 $^{\circ}\text{C}$ annealing, the semiconducting behavior could be observed. Along with increasing of annealing temperature to 600 $^{\circ}\text{C}$, the on/off ratio can be increased to $\approx 10^5$ and the mobility is $\mu = 0.12 \text{ cm}^2/\text{Vs}$. However, a high off-current was noticed due to high amount of point defect in ZnO [7]. In the other hand, as IGZO thin film irradiated with DUV, the In and Ga ions could be embedded inside the Zn(M-O-M) matrix. The IGZO TFT annealed at 300 $^{\circ}\text{C}$ exhibited a better transfer characteristic than ZnO TFT annealing at 600 $^{\circ}\text{C}$, as shown in Fig. 3b). The on/off ratio of $\approx 10^6$, the mobility of $\mu = 1.1 \text{ cm}^2/\text{Vs}$, and steady off-current can be seen. This result demonstrates the potential for producing mixture of metal oxide devices by using metal MOCs-based precursors.

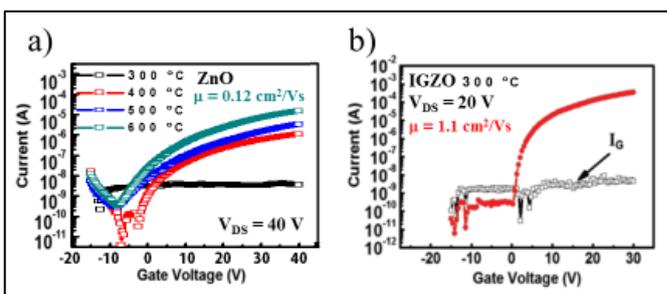


Fig. 3 Transfer curve of DUV patterned a) ZnO devices annealing in different temperature b) IGZO device annealing at 300 $^{\circ}\text{C}$.

3. Conclusions

We demonstrated the potential of using small molecular organic ligand as a versatile method to prepare photo sensitive metal oxo-cluster. Using this MOCs enables producing metal oxide nanostructure by DUV irradiation. Furthermore, by doping different material in to the basic MOCs matrix, the potential of mixture of metal oxide can be imagined.

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