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The effect of Ar plasma etching time on the microstructure, optical and photoelectric properties of CdZnTe films

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ABSTRACT

In this work, Ar plasma etching was performed to polycrystalline CdZnTe thick films grown from close-spaced sublimation method. The effect of Ar plasma etching time on the microstructure, optical and photoelectric properties of CdZnTe films were investigated by using AFM, XRD, UV–visible spectrophotometer and current-voltage characterization system. The results showed that proper plasma etching time can significantly improve the surface roughness and passivate the CdZnTe film surface, leading to less surface leakage current and higher photo-response of the Au/CdZnTe/FTO photo-conductive structure. Its photo-response sensitivity under 281 nm UV irradiation increases with one order of magnitude after 5 min' etching.

1. Introduction

CdZnTe, as an excellent II-VI semiconductor compound, has a larger band-gap and atomic number, and can operate at room temperature and has greater stopping power and strong anti-radiation for radiation detectors [1–3]. Hence, CdZnTe-based devices have a wide range of applications in aerospace, space science, medical equipment, airport and port security, nuclear waste detection and other nuclear technology [4–5]. Compared with the single crystal growth process, polycrystalline CdZnTe has simple preparation process, lower cost, high feasibility of batch growth, and is suitable for the preparation of large area of flat panel detector [6–7].

Previous work on CdZnTe films showed that surface treatment was one of dominant factors affecting the performance of CdZnTe detectors [8–10]. The surface status greatly influences the leakage current, contact property and performance of the detectors. So, it is necessary to obtain CdZnTe surface with high-quality. In general, the Br–MeOH (BM) solution is widely used for the etching of mechanically damaged layers and the removal of the native Te oxides of CdTe and CdZnTe bulk crystals, which can improve the flatness of the surface [11]. However, BM etching is a kind of wet chemical process, and bromine-based etchants are toxic and harmful. The plasma etching is commonly used in the microelectronic technology, especially for conventional silicon-based electronic devices, and it is a physical dry etching process, which can overcome the limitations of wet etching.

Min et al reported the effect of hydrogen plasma treatment on CdZnTe crystals and found that the hydrogen plasma etching could reduce the surface point defects and leakage current, and improve the performance of the electrode contacts [12]. Robert C et al pointed that CdZnTe was much more susceptible to evolving surface roughness under H_2/Ar plasma exposure than CdTe [13]. These findings indicated that plasma treatment had an important effect on properties of CdZnTe surface. However, the effect of plasma etching on CdZnTe photoelectric properties has not been involved. Moreover, the previous studies only focused on CdZnTe single crystal, and the plasma treatment on polycrystalline CdZnTe thick film has been rarely reported.

In this work, Ar plasma treatment with different etching time is carried out on the surface of CdZnTe thick films. The effect of plasma etching process on morphological, structural, optical and UV photoelectric properties of CdZnTe films was investigated in detail.

2. Experimental details

In this paper, CdZnTe films were deposited onto the SnO_2: F-coated substrates (FTO, 2 cm × 2 cm) by close-spaced sublimation (CSS) under vacuum condition. Prior to film deposition, the substrates were cleaned in acetone, ethanol and deionized water with ultrasonic cleaning for 15 min, respectively. The CdZnTe powder (99.999% purity) was used as the sublimation source and the temperature of sublimation source and substrate were kept at 650 °C and 400 °C, respectively. The distance between source and substrate was 4 mm, and the chamber pressure was 5.4 Pa. The deposition time was 3 h, and the thickness of CdZnTe films obtained was about 270 μm confirmed by using cross-section image of SEM. Subsequently, CdZnTe films were manually polished for 15 min using polishing liquid which was formulated by 0.5 μm alumina powder with deionized water in proportion of 1:10. Then the CdZnTe films were treated with Ar plasma in a sputtering

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system for 0, 2, 5, and 10 min, respectively. The Ar plasma etching power was 70 W. To evaluate the effect of plasma treatment on the opto-electrical properties of CdZnTe films, Au/CdZnTe/FTO photo-conductive structures with Au interdigital electrodes were fabricated. 150 nm thick Au electrodes were prepared by vacuum evaporation, and the electrode width and spacing was 1 mm and 0.5 mm, respectively.

The structure of the films was evaluated by X-ray diffraction (XRD) with a resolution of 0.02° (D/MAX-3C, $CuK_{\alpha} = 0.15406$ nm). The reflectivity of CdZnTe thick film was measured using Jasco UV-570 spectrophotometer with the wavelength from 300 to 1800 nm. The morphology of the films was investigated with atomic force microscopy (AFM, Bruker Multimode 8). The electrical properties of Au/CdZnTe/FTO photo-conductive structure were measured using a Keithley 4200/SCS digital semiconductor characterization system and a PTI optical system.

3. Results and discussion

Fig. 1 shows the XRD patterns of CdZnTe films with different Ar plasma treatment time, and all films reveal obvious (111) preferred orientation. It can be figured out that untreated sample shows the strongest diffraction peak, and with the increase of the Ar plasma etching time, the (111) diffraction peak intensity exhibits different degrees of decline. The XRD data of CdZnTe films treated with different etching time are listed in Table 1. It can be observed that the full width at half maximum (FWHM) of CdZnTe (111) diffraction peak becomes large as the etching time increases from 2 min to 5 min and then becomes small at etching time of 10 min, while compared with the untreated sample there is a marked increase.

The grain size is also calculated from the XRD pattern using Scherrer's formula equation $D = 0.9\lambda / \beta\cos\theta$ [14], where D is the grain size of the CdZnTe films, λ is the wavelength of the X-rays ($CuK_{\alpha1}$ 1.54056 Å), β is the broadening of the diffraction line measured at FWHM, and θ is the diffractive angle. The calculation results show that the grain size of untreated sample is 72.1 nm, while those with Ar plasma etching are 50.2 nm, 45.3 nm and 62.6 nm for 2 min, 5 min and 10 min, respectively. This result indicates the grain size of sample treated by 5 min is the smallest, which provides a smooth surface, and is favored to the formation of good ohmic contact. The changes of grain size after Ar plasma etching process may be one of the reasons for the varying of FWHM as shown in Table 1.

From XRD results from the inset in Fig.1, CdZnTe(111) diffraction peak also shows a tendency shifting to lower angles with increasing of treatment time, which may be caused by the variety of Zn content on the surface of CdZnTe after different Ar plasma treatment time [15]. This is consistent with the obtained results from Energy Dispersive

Table 1
The XRD data of CdZnTe films with different Ar plasma etching time.

Etching time (min)	2θ (degree)	d (Å)	a (Å)	(111) Intensity (a.u.)	FWHM (degree)	D (nm)
0	24.04	3.6982	6.4055	31,576	0.195	72.1
2	24.04	3.6987	6.4063	11,371	0.279	50.2
5	23.98	3.7079	6.4223	26,201	0.309	45.3
10	23.86	3.7264	6.4543	23,575	0.224	62.6

Spectrometer (EDS) characterization (not shown here). The Zn content in CdZnTe film was 6.47%, 7.33%, 10.25% and 13.02% for films with 0, 2, 5 and 10 min etching, respectively.

The optical reflectivity (R) of CdZnTe films treated with different time are identified by Jasco UV-570 spectrophotometer in the wavelength range from 300 to 1800 nm, shown in Fig. 2. It can be concluded that the reflectivity is small in the UV–visible region, while sharply changes at near 800 nm, which corresponds to the absorption edge of CdZnTe. In the visible light region (400–800 nm), the reflectivity is less than 30%, that means most of the incident photons enter the CdZnTe films, and then contributes to photoelectric conversion. With the increasing of etching time, the reflectivity shows a decrease trend in the wavelength range of 300 to 1800 nm. Particularly, the reflectivity declines rapidly in short-wavelength, from 30% to 5%. This probably is the result of changed properties of the film surface after plasma treatment.

Fig. 3 and Fig. 4 present the topography and roughness of the CdZnTe samples obtained from AFM measurement, where Rq is the root-mean square [16]. It demonstrates that both the roughness and grain size decrease with the increasing plasma etching time from 0 min to 5 min and then increase with the etching time of 10 min. The film with smoother surface and smaller grain size is obtained with 5 min etching, which is consistent with the XRD results.

The as-deposited sample shows a rough and uneven surface. However, with 2 min etching, the fluctuation and roughness of CdZnTe grow smaller, and the roughness drops sharply to 0.179 nm after 5 min etching. The improvement of roughness can offer a superior surface for the deposition of electrodes and helps to improve the properties of Au/CdZnTe/FTO photo-conductive structure. With the 10 min etching, the surface morphology becomes bad slightly along with the roughness, indicating that too long time treatment may cause further damage to the surface.

To evaluate the effects of Ar plasma treatment on electrical properties of CdZnTe films, the dark-current and UV photo-current of Au/CdZnTe/FTO samples were measured at a bias voltage from −20 V ± 20 V, as shown in Fig.5 and Fig. 6. The photo-current measurement was performed under 281 nm UV irradiation. It can be found in

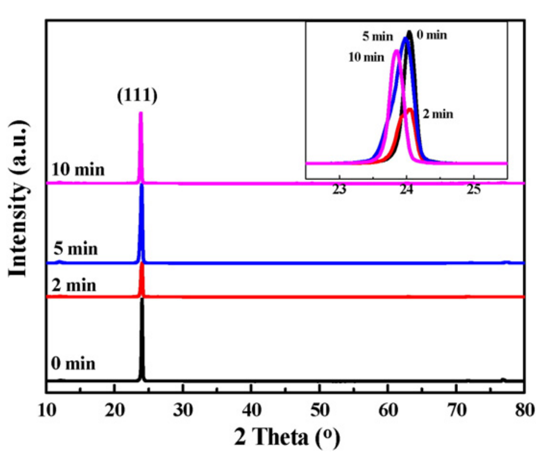

Fig. 1. XRD patterns of CdZnTe films with different Ar plasma etching time. The inset gives the CdZnTe (111) diffraction peak.

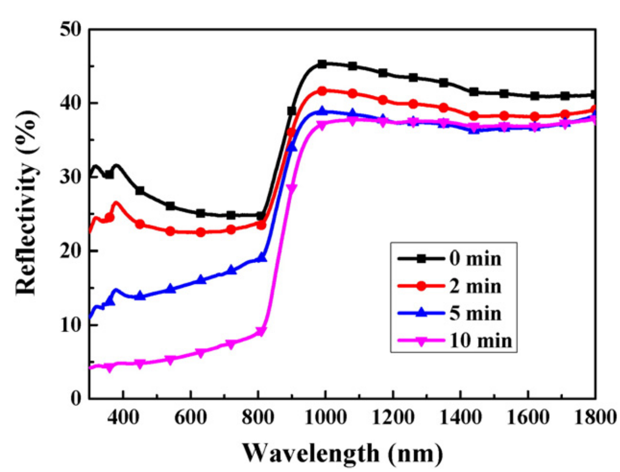

Fig. 2. The reflectivity spectra of CdZnTe thick film with different Ar plasma etching time.