As one of the most promising wide bandgap semiconductor, β-Ga2O3 has become increasingly important to solar blind photodetector and power devices technologies because of its promising properties.1–4 β-Ga2O3 is a direct gap semiconductor with bandgap of about 5.0 eV,5 which is the second largest after that of diamond. Ga2O3 β-bandgap can be adjusted by Al or In doping. Therefore, the properties of β-Ga2O3 make it a promising candidate for short wavelength optoelectronic devices photodetectors.6–10

Various reports have been conducted on the growth of Ga2O3 thin films and the fabrication of solar-blind UV detectors. Polycrystalline Ga2O3 thin films on (0 0 0 1) sapphire substrates by using sol–gel method,17 Ga2O3 thin films on c-plane sapphire substrates were fabricated by plasma-assisted MBE.18 Except for the above methods, the Ga2O3 films also have been grown by mist chemical vapor deposition19 and sputtering20,21 and other methods. Materials fabrication and device technology would be more commercially attractive if inexpensive materials fabrication and device testing system (SolarCellScan 100). I-V of the as-synthesized device was measured by the electrochemical workstation (Corretst, CS350) with a three electrodes system.

Results and Discussion

Figs. 1a and 1b show the XRD θ-20 patterns of the as-deposited and 500, 600, 700, 800 and 900°C-annealed Ga2O3 films, respectively. As-deposited films grown at RT shows several broad bands except for sapphire (006) diffraction peak, which indicates the as-deposited thin film is mostly amorphous. Increasing the annealing temperature from 500°C to 900°C, three diffraction peaks located at 18.95°, 38.40° and 59.19° indexed to (201), (402) and (603) were all attributed to β-Ga2O3 after annealing from when temperature higher than 500°C. Besides β(402) peak, β(400), β(202) and αβ(712) peak could be observed at annealed sample at 900°C. During the annealing process, one part of thermal energy can be provided to rearrange the atoms. Meanwhile, the other part of thermal energy could...
XRD patterns of Ga₂O₃ films prepared by magnetron sputtering. (a) as-grown sample; (b) annealed samples. The peak intensity and full width at half maximum (FWHM) of β(¯402) peak as a function of annealing temperature are shown in Fig.2a. The FWHM of β(402) peak decreased with increasing annealing temperature, which is attributed to larger driving energy to migrate atoms to more suitable lattice sites and result in more high crystallinity. The average grain size of thin film can also be predicted by Scherer formula:

\[ D = 0.89\lambda/\beta\cos\theta \]  

where \( \lambda \) is the wavelength of X-ray, \( \theta \) is the Bragg diffraction angle and \( \beta \) is the FWHM of the highest peak (402) (in radian). The grain size increased gradually as annealing temperature increasing from 500°C to 900°C in Fig.2b, indicating the improvement of the film quality.

Optical transmittance spectra of the as-grown and annealed Ga₂O₃ thin films at different annealing temperature are shown in Fig.3. The transmittance in the visible range is higher than 90% for all samples. The optical bandgap of a semiconductor film is an important indicator for the application of an optoelectronic device, which is calculated from the following formula.

\[ \alpha h\nu = C(h\nu - E_g)^{1/2} \]  

where \( \alpha \) is the absorption coefficient, \( h\nu \) is the photon energy and \( C \) is a constant. According to Tauc plot, the optical energy gap could be estimated by extrapolating the linear sections to the axis of energy. As shown in Fig. 3b, the optical bandgap of the as-grown film is 4.02 eV, which is far smaller than the reported value for the β-Ga₂O₃ films. The optical bandgap of annealed Ga₂O₃ films shifts to low energy from 5.04 eV to 4.19 eV as the annealing temperature increasing from 500°C to 900°C. As discussed in the XRD results, higher post-annealing temperature would increase the size of the grain size, resulting in quantum confinement effect weakening and bandgap shrinking. As-grown amorphous film has lower optical bandgap due to more defects near bandgap.

In order to measure the photoelectrical response of Ga₂O₃ thin films, Au electrodes were deposited on the films to construct the MSM type photodetector using a shadow mask, as shown in the inset of Fig. 4a. Fig. 4 shows I-V characteristics of the fabricated photodetectors based on as-grown amorphous thin film with (a) the linear and (b) logarithmic coordinate. It is confirmed that ohmic contacts have been formed at the interface between amorphous film and metal rather than Schottky contacts. The currents in dark and under 365 nm are only 0.1 pA and 1.1 pA under the bias voltage of 20 V, which suggests the amorphous Ga₂O₃ thin film has very weak sensitivity to 365 nm light. Photoreponse spectrum could not be detected due to small value of \( I_{\text{light}}/I_{\text{dark}} \). This is because electrons cannot jump from the valence band to conduction band under the excitation of 365 nm light. In contrast, the current shows a sharp jump as the device is exposed to the 254 nm light, and the photocurrent increases to 0.1 nA at 20 V. Spectral responses of the photodetector made from the amorphous Ga₂O₃ thin films is shown in Fig. 5. The photo-current gradually increases when the wavelength of the illuminated light is scanned from 300 nm and reaches its peak value at 256 nm and then falls gradually. The responsivity of the photodetector is 122.7 μA/W at 256 nm and is two orders of magnitude higher than that at 400 nm, which is lower than the reported value for the β-Ga₂O₃ films.
Figure 3. (a) Transmittance spectra for as-grown and annealed Ga$_2$O$_3$ films; (b) Square of the absorption coefficient as a function of photon energy for as-grown and annealed Ga$_2$O$_3$ films.

indicates that the amorphous Ga$_2$O$_3$ thin film has potential application for solar-blind photodetector.

Fig. 6 plots the $I-V$ curves of annealed samples in the dark and under 254 nm light with log-linear scale. The dark current of all the samples increased with the bias voltage in the range of 0 V–30 V. For the film annealed at 500°C, the dark current reached 0.02 nA at a bias voltage of 30 V. As annealing temperature rising from 500°C to 900°C, the dark current dropped by about one orders of magnitude, reaching almost 1 pA level at the bias voltage of 30 V. The decrease in the dark current of the films might be ascribed to the enhancement in the film crystallization quality under higher post-annealing temperatures. However, photocurrent under 254 nm light has the same level with dark current, no obvious photoresponse could be found for polycrystalline $\beta$-Ga$_2$O$_3$ annealed at high temperature. Improving crystal quality and increasing photoconductivity are needed to obtain the photoresponse with polycrystalline $\beta$-Ga$_2$O$_3$ films.

From the above analysis, amorphous film shows low crystal quality and more defects than annealed polycrystalline films. However, photoresponse with 254 nm light could be found in the amorphous film instead of annealed films. The XPS measurements have been performed to investigate the compositions and chemical states of Ga$_2$O$_3$ film. The PL spectra of the samples exhibit two characteristic bands at blue and green regions excited by He-Cd laser with the wavelength focused at 325 nm, as shown in Fig. 8. Apparently, the UV emission peak originated from Ga$_2$O$_3$ band edge could not be detected due to excitation energy less than the bandgap. However, the emission from the defects could be observed clearly. The blue emission band centered at 430 nm is attributed to the recombination of an electron on a donor and a hole on an acceptor, where the origin of the donor is an oxygen vacancy and the acceptor is a gallium vacancy or gallium–oxygen vacancy pair. The green emission band centered at 550 nm is originated from the recombination of an electron on a donor and a hole on an acceptor, which is called the donor-acceptor pair (DAP) recombination mechanism. The donor may be formed by oxygen vacancies and interstitial Ga, and acceptor is composed of gallium vacancies or gallium–oxygen vacancy.
Figure 5. Spectral response of the photodetector made from the as-grown amorphous film. The inset shows the variation of photocurrent with wavelength.

Vacancy pairs ($V_{Ga}, V_{O}$). The peaks at 679 nm and 693 nm are corresponding to sapphire substrate, and both samples peaks are normalized by higher substrate peak at 679 nm. The blue and green emission bands are both related to the oxygen vacancies defects. The intensities of these two bands in the as-grown amorphous film are much stronger than those in annealed films, which also confirm that amorphous film have more oxygen vacancies than that of polycrystalline $\beta$-Ga$_2$O$_3$.

The effect of oxygen vacancies on the performance of photodetectors could be summarized as a schematic graph in Fig. 9. The density of oxygen vacancies is high in amorphous film as indicated by XPS results, which will modify the contacts from schottky to ohmic contacts induced by the Fermi level of amorphous Ga$_2$O$_3$ pinned close to the oxygen vacancies defect level. Consequently, the narrow depletion region will be formed at the interface making it susceptible to electron tunneling, thus leading to an ohmic-type electron transport. On the other hand, fewer oxygen vacancies implied lower doping concentration and led to a wider depletion region that hindered the charge

Figure 6. Current-voltage characteristic of the MSM junction made from annealed film in dark and with 254 nm illumination, annealing temperature is (a) 500°C; (b) 600°C; (c) 700°C; (d) 800°C; (e) 900°C; (f) The variation of current with annealing temperature.

Figure 7. O1s XPS spectra of the as-grown and annealed Ga$_2$O$_3$ films.
transportation. By adjusting the concentration of oxygen vacancies of amorphous Ga$_2$O$_3$, amorphous films have great potential for high-performance photodetection.

Conclusions

Gallium oxide thin films were deposited by radio frequency magnetron sputtering technique at room temperature. The as-grown Ga$_2$O$_3$ thin films show amorphous characteristic. The responsivity of the photodetector based on as-grown amorphous film is 122.7 $\mu$A/W with a peak wavelength of 256 nm and the ultraviolet (UV)-to-visible rejection ratios were 100. Annealed film are polycrystalline with monoclinic structure, which have no obvious photosresponse for deep ultraviolet light. The difference of photosresponse between amorphous and polycrystalline film are attributed to high density of oxygen vacancies in amorphous films. The oxygen vacancies close to the metal–semiconductor interface tend to influence the electron transportation induced by the Fermi level of amorphous Ga$_2$O$_3$ pinned close to the oxygen vacancies defect level. The narrow depletion region will be formed at the interface making it susceptible to electron tunneling. For higher oxygen vacancy density, more electrons could tunnel through the interface barrier and be injected into the semiconductor and induce higher photosresponse in amorphous film.

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