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ARTICLE

Preparation of ITO Coating on PMMA by High-power Pulse Magnetron Sputtering

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Abstract: ITO coatings were deposited on polymethyl methacrylate (PMMA) by high-power pulse magnetron sputtering (HPPMS). The effects of HPPMS on the coatings under different parameters were investigated, and the phase, bonding strength, transmittance and resistivity were characterized by XRD, scratch tester, spectrophotometer and Hall test platform, respectively. The results show that phase, bonding strength, transmittance and resistivity are affected by pulsed bias and flow rate ratio of hydrogen and argon. With increasing the pulsed bias, the bonding strength becomes better, and the best bonding strength is 56.5 N when pulsed bias is 240 V. With increasing the pulsed bias from 0 V to 160 V, the grain size gets bigger, the transmittance becomes better (increasing from 82.24% to 89.82%) and the resistivity also becomes better (decreasing from 0.006 571 to 0.000 543 Ω·cm). With increasing the flow rate ratio of hydrogen and argon from 0 to 0.05, the transmittance becomes worse (decreasing from 89.82% to 56.12%). With increasing the flow rate ratio of hydrogen and argon from 0 to 0.03, the resistivity becomes better (decreasing from 0.000 543 to 0.000 212 Ω·cm). With increasing the flow rate ratio of hydrogen and argon from 0.03 to 0.05, the resistivity becomes worse (increasing from 0.000 212 to 0.000 373 Ω·cm).

Key words: ITO coatings; high-power pulse magnetron sputtering; PMMA; pulsed bias; flow rate ratio of hydrogen and argon

Polymethyl methacrylate (PMMA) is commonly named as organic glass and has excellent characteristics of high visible light transmittance, mechanical strength, corrosion resistance and easy processing. The devices produced by ITO (indium tin oxide) film-coated PMMA have a lot of outstanding photoelectric properties, such as high visible light transmittance, infrared reflectivity, UV absorptivity and conductivity, and have a widespread application prospect in the field of aerospace, weapons, equipment and industrial production[1]. There are many preparation methods of ITO coating on the PMMA, such as magnetron sputtering, chemical vapor deposition, vacuum evaporation, sol-gel method and spray pyrolysis[2]. The coatings that are prepared by magnetron sputtering are uniform, fast film forming and stable processing, so most practical projects use magnetron sputtering to prepare the ITO coating on the PMMA[3]. In usual preparation process of ITO coating, the substrates temperature is more than 200 °C at least and subsequent annealing is conducted to guarantee photoelectric properties and bonding strength. As PMMA is not heat-resistant, substrate temperature is required to be below 100 °C. So the photoelectric properties and bonding strength of ITO coating prepared on PMMA are not good enough. The HPPMS (high-power pulse magnetron sputtering) has high ionization rate and high ion current density compared to magnetron sputtering, it produces the high density bombardment ion on coatings[4], and the prepared coating has better quality at a temperature below 100 °C. From all appearances, it is a valuable research for obtaining ITO coating on the PMMA by HPPMS. According to the researchers, the HPPMS substrate pulsed bias is important for coating properties, and the hydrogen is important for photoelectric properties of semiconductor coatings (ITO coating is semiconductor coatings). In the present, the influencing factors of coating properties (such as bonding strength and photoelectric properties) including HPPMS substrate pulsed bias and flow rate ratio of hydrogen and argon were investigated.

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1 Experiment

The PMMA substrate samples of 40 mm×40 mm×5 mm dimension were cleaned in the alcohol medium and thoroughly dried. The ITO coating was deposited by HPPMS on the PMMA substrate. In the experimental process, target was high purity ITO (In_2O_3:Sn_2O_3=9:1), base pressure of chamber was 2×10^{-3} Pa, working pressure was 0.5 Pa, target-substrate separation was 10 cm, coating thickness was about 500 nm, the substrate pulsed bias was in the range of 0~240 V, and the flow rate ratio of hydrogen and argon was 0~0.05.

The phase was characterized by X-ray diffraction with Ni filtered Cu Kα radiation (λ= 0.154 18 nm) and scintillation detector within 2θ range of 15°~70°. The film-substrate cohesion was investigated by scratch tester under different loads (30, 40, 50, 60 N). After deducting the influence of PMMA substrate on transmittance, the ITO coating transmittance was tested by spectrophotometer in the wavelength range of 300~800 nm with the same coating thickness (about 500 nm). The coating square resistance was tested by Hall test platform, and the instrument also tested the carrier density and the Hall mobility.

2 Results and Discussion

2.1 Phase structure of coating

As can be seen from Fig.1, the diffraction peaks corresponding to 21.2°, 30.8°, 35.7°, 51.2°, 60.8° show the presence of In_2O_3 phase under different pulsed bias, and the preferred orientation of ITO deposits is (222). Sn_2O_3 phase cannot be found in Fig.1, because Sn_2O_3 enters the In_2O_3 crystal lattice and forms a uniform solid solution structure[5].

As can be seen from Fig.1, the half width of In_2O_3 phase diffraction peak decreases and the grain size gets bigger, and meanwhile the preferred orientation of (222) is improved as pulsed bias changes from 0 V to 160 V. When the pulsed bias is 160 V, the half width of diffraction peak is smaller and the grain size is bigger. When the pulsed bias is 240 V, compared to at 160 V pulsed bias, the preferred orientation is unchanged but the half width of diffraction peak is higher and the grain size is smaller.

With increasing the pulsed bias from 0 V to 160 V, the sputtering particle energy is higher, that is to say, the substrate surface particles have higher energy, so the deposition quality is better and the grain size is bigger. However, the sputtering particle energy is too high under 240 V pulsed bias, the sputtering effects is obvious, the particles bombard on coatings, affecting crystal growth, and the grain size becomes smaller.

2.2 Bonding strength of coating

In the scratch experiment, five samples were chosen from every kind of different parameters for the test. The load at which the film peels off from sample is considered as the critical load of coatings, and it is usually considered as the bonding strength. The critical load results measured by the adhesion test are characteristic values for each sample.

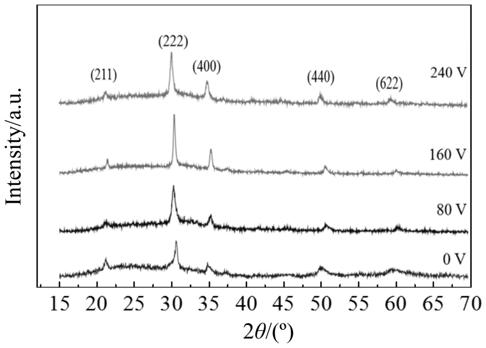

Fig.1 XRD patterns of ITO coatings at different pulsed bias

At a lower load of 30 N, there are smooth continuous scratches on the surface of all samples without any transverse crack. When the load is 40 N, there is transverse crack on the surface of some original samples, and few samples present film peeling. When the load is 50 N, some samples present film peeling. With increasing the load to 60 N, all samples present film peeling. After analyzing, the best bonding strength of coating is about 56.5 N, which is good enough for engineering application.

As can be seen from Fig.2, the bonding strength becomes better with changing substrate pulsed bias from 0 V to 240 V. With increasing substrate pulsed bias, the ion bombarding energy increases and there are more ions implantation into the substrate, and then a transition layer is obtained on the surface of substrate, so the coating stress releases. Therefore, the bonding strength is the highest as the substrate pulsed bias is 240 V. As the ion bombarding energy is too lower, there is no transition layer and ion implantation effect on the substrate surface, and the bonding strength is poor because of the coating stress.

2.3 Photoelectric properties of coating

2.3.1 Transmittance

As can be seen from Fig.3, the average transmittance (T) is above 82% at different pulsed bias in the visible range, which

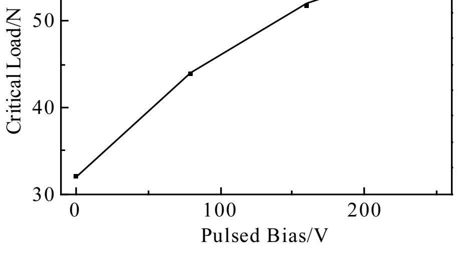

Fig.2 Critical load of simples at different pulsed bias

shows that the average transmittance of ITO coatings is well. With changing substrate pulsed bias from 0 V to 80 V, the average transmittance has a very large improvement (from 82.24% to 87.40%), reaching 5.16%. With further increasing pulsed bias from 80 V to 160 V, the average transmittance improves less and even decreases (from 89.82% to 86.87%) when the pulsed bias changes from 160 V to 240 V.

The coating crystallinity can affect transmittance[6], as the transmittance is better with higher crystallinity within a certain range. The crystallinity has obvious improvement (as can be seen from Fig.1) with changing the pulsed bias from 0 V to 160 V, so the transmittance is greatly improved. However, when the pulsed bias reaches 240 V, the grain crystallinity is decreased, so the transmittance is worse.

As can be seen from Fig.4, the average transmittance is worse with increasing the flow rate ratio of hydrogen and argon at a fixed pulsed bias (160 V). In the sputtering process, first-principle calculation indicates that H can occupy the interstitial positions or replace the O positions in ITO[7,8] , which reduces the O content of coatings and increases the oxygen vacancy content. With increasing the flow rate ratio of hydrogen and argon within a certain range, the oxygen vacancy content increases, which means that crystal defect increases[9]. The more crystal defects, the worse the transmittance in a certain flow rate ratio of hydrogen and argon range[10]. When flow rate ratio of hydrogen and argon reaches a certain amount, the H reduction increases in the coatings and the ITO metallicity is strengthened, so the transmittance is worse.

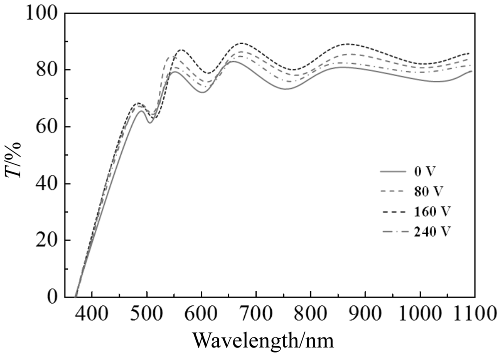

Fig.3 Transmittance of ITO coatings at different pulsed bias

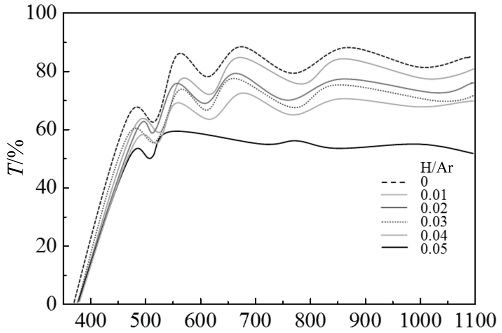

Fig.4 Transmittance of ITO coatings at different flow rate ratio of H/Ar

2.3.2 Resistivity

As can be seen from Fig.5, the coating resistivity first decreases and then increases with increasing the pulsed bias under pure argon conditions. The coating resistivity is affected by the carrier density and Hall mobility. Generally speaking, the coating resistivity is lower at the higher carrier density or Hall mobility[11]. From the XRD result, with changing the pulsed bias from 0 V to 160 V, the grain size gets bigger, that is to say, the less the grain boundary, the smaller the grain boundary scattering effects, and the higher the Hall mobility[12,13]. Meanwhile, the carrier density just has a little change in this process, and the coating resistivity, which is mainly affected by the Hall mobility, is decreased. When the pulsed bias is 0 V, the coatings resistivity is 0.006 571 Ω·cm. When the pulsed bias is 160 V, the coating grain size is the biggest and the coating resistivity is the best (0.000 543 Ω·cm). When the pulsed bias is 240 V, the smaller the coating grain size, the greater the grain boundary scattering, and the higher the coating resistivity.

As can be seen from Fig.6, with increasing the flow rate ratio of hydrogen and argon at a fix pulsed bias (160 V), the coating resistivity first decreases (from 0.000 543 to 0.000 212 Ω·cm with increasing flow ratio from 0 to 0.03) and then increases (from 0.000 212 to 0.000 373 Ω·cm with increasing flow ratio from 0.03 to 0.05), and the Hall mobility first increases (flow ratio is 0~0.02) and then decreases (flow ratio is 0.02~0.05), and the carrier density increases (flow ratio is 0~0.05).

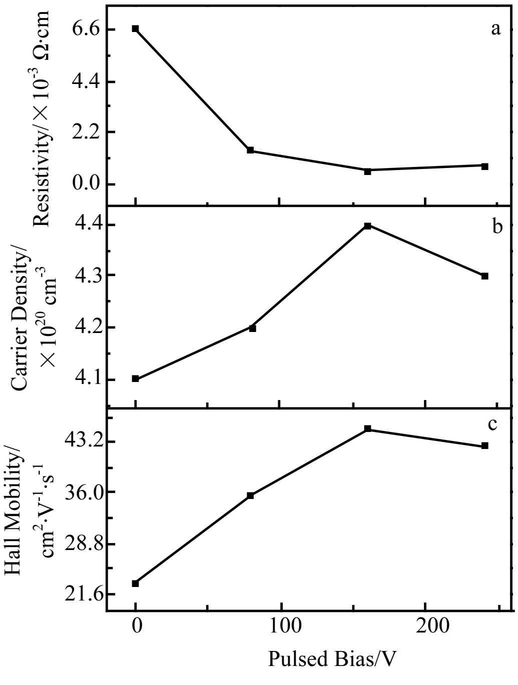

Fig.5 Resistivity (a), carrier density (b), and the Hall mobility (c) of ITO coatings at different pulsed bias

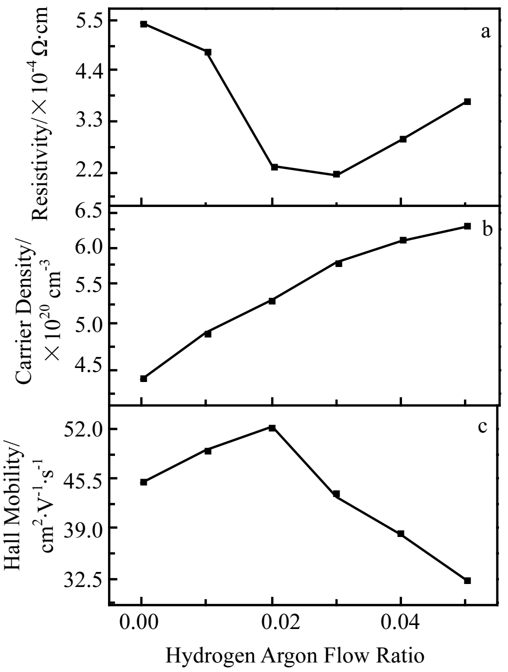

Fig.6 Resistivity (a), carrier density (b), and the Hall mobility (c) of ITO coatings at different flow rate ratios of hydrogen and argon

The ITO coatings are semiconducting films, so the coating resistivity is affected by the carrier density and Hall mobility. During the sputtering process in the H atmosphere, H will occupy interstitial positions of ITO (In_2O_3/Sn_2O_3), in other words, H doping in ITO improves the carrier density[14]. After H is doped in ITO, the H passivates the grain boundary and reduces the grain boundary scattering in carrier transport process, and the Hall mobility that is closely related to scattering increases. However, if H doping in ITO is excessive, H will become the new scattering center, and the Hall mobility decreases. When flow rate ratio of hydrogen and argon changes from 0 to 0.02, the carrier density and Hall mobility increase, the coating resistivity decreases and the change ratio is higher. When flow rate ratio of hydrogen and argon changes from 0.02 to 0.03, the carrier density increases but the Hall mobility decreases, and the coating resistivity decreases with a small change ratio. When flow rate ratio of hydrogen and argon changes from 0.03 to 0.05, the coating resistivity increases, that is to say, the H is excessive and the flow rate ratio of hydrogen and argon is too high.

3 Conclusions

1) The pulsed bias can change microstructures of coatings. Within a certain range (from 0 V to 160 V), higher pulsed bias can propel the grain growth.

2) With increasing the pulsed bias, the bonding strength becomes better, and the optimal bonding strength is 56.5 N at a pulsed bias of 240 V.

3) The pulsed bias and flow rate ratio of hydrogen and argon can affect the transmittance of coatings. The transmittance becomes better (increasing from 82.24% to 89.82%) with increasing the pulsed bias from 0 V to 160 V. The transmittance becomes worse (decreasing from 89.82% to 56.12%) with increasing the flow rate ratio of hydrogen and argon from 0 to 0.05.

4) The pulsed bias and flow rate ratio of hydrogen and argon can affect the resistivity of coatings. The resistivity becomes better (decreasing from 0.006 571 to 0.000 543 Ω·cm) with increasing the pulsed bias from 0 V to 160 V. The resistivity becomes better (decreasing from 0.000 543 to 0.000 212 Ω·cm) with increasing the flow rate ratio of hydrogen and argon from 0 to 0.03, and then the resistivity becomes worse (increasing from 0.000 212 to 0.000 373 Ω·cm) with increasing the flow rate ratio of hydrogen and argon from 0.03 to 0.05.

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PMMA表面高功率脉冲磁控溅射制备ITO涂层

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摘　要：采用高功率脉冲磁控溅射技术在 PMMA 基体上制备了 ITO 涂层。利用 XRD、SEM 对涂层进行了相结构的分析，并进行了划痕实验、光电性能测试。结果表明：偏压、氢氩流量比等工艺参数对涂层的相结构、膜基结合力、光电性能均有影响。增大偏压，膜基结合力将增强，偏压达到240 V时，膜基结合力最好（56.5 N）。偏压由0 V增加到160 V的过程中，涂层晶粒增大，透射率变高（由82.24% 增至 89.82%），电阻率变低（由0.006 571 减至 0.000 543 Ω·cm）。当氢氩流量比由0增至0.05，透射率变低（由89.82%减至56.12%)。氢氩流量比由0增至0.03，电阻率变低（由0.000 543减至0.000 212 Ω·cm）；氢氩流量比由0.03增至0.05，电阻率变高由0.000 212 增至0.000 373 Ω·cm）。

关键词：ITO涂层；高功率脉冲磁控溅射；PMMA；脉冲偏压；氢氩流量比

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