太陽電池用透明導電膜としてのZnO:Alの特性と信頼性

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学位授与年月日　平成２６年３月２６日
学位授与の根拠法規　学位規則第４条第１項
研究科，専攻の名称　東北大学大学院工学研究科（博士課程）知能デバイス材料学専攻
学位論文題目　太陽電池用透明導電膜としての ZnO:Al の特性と信頼性
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論 文 内 容 要 旨

In recent years, because of concerns about the pollution and safety related to fossil fuel and nuclear energy, solar cells have received much attention. However, the high price of solar cells still remains as a main problem for wide-spread use as commercial products.

Silicon cells are the most widely used solar cells in the market. Among various types of the silicon cells, HIT (heterojunction with intrinsic thin layer) cells are known to have the best conversion efficiency. The HIT cells are composed of a n-type silicon substrate, an amorphous intrinsic thin layer, and an amorphous p-type or n+-type thin layer. On top of this, a transparent conducting oxide (TCO) layer is formed to effectively collect photo-generated carriers. The collected carriers then flow out via metals lines. The top metal lines use thermoset-type silver paste at present, due to its low resistivity. However, the high price of silver also became an obstacle to low price solar cells. To replace silver, copper can be a promising material for the top metal lines. Meanwhile, ITO (Indium-doped Tin Oxide) is the most widely used TCO material, due to its good conductivity and high transparency. However, ITO is an expensive material and is desired to be replaced with alternative TCO materials. Meanwhile,

Among various TCOs, Al-doped ZnO (AZO) is one of the most promising materials. AZO is nontoxic and available at much lower cost. It also has good thermal stability and similar electrical and optical properties compared to ITO. Therefore AZO will be the main target of TCO material for low price solar cells in this study.

In consideration of AZO for solar cells, some problems need to be solved. First, the TCO films are necessary to ensure a good electrical contact with underlying Si substrates. Solar cells are exposed to various heating conditions through the fabrication process and through their long-term usage under a strong sunshine. The heat exposure may induce interfacial reaction between Si and AZO. Depending on a reaction layer formed at the interface, light may not effectively reach a p-n junction and generated carriers may be trapped at the reaction layer. These effects would cause the deterioration of solar cell efficiency. Therefore, the reaction behavior and electrical properties of AZO/Si are one of the objectives of this research. Second, in the case of hetero-junction silicon solar cells, metal lines are formed to collect photo-induced electrons via a TCO layer, and are required to have good adhesion strength with the TCO layer. Therefore in this study, we investigated the adhesion strength of copper with AZO using a scratch method. Third, for copper used for metal lines, annealing is performed in production process. However, copper will diffuse into Si easily, therefore the diffusion barrier property of AZO between Cu and Si was investigated.

In Chapter 3, the results of the conduction property of AZO thin film are shown and discussed. ZnO thin films and AZO thin films were prepared by RF sputtering, and their electrical properties were investigated. The ZnO results showed that the thin film prepared by sputtering at 400°C had a low resistivity. The post annealing of ZnO thin films also lead to the reduction of resistivity, especially when they were annealed at low oxygen pressure. The AZO results showed that, lower sputtering power and higher Ar flow rate could reduce the resistivity of AZO thin film prepared by room temperature sputtering.

In Chapter 4, interface reaction between AZO and Si, and its effects on optical and electrical properties of AZO films were investigated. AZO films with 100nm thickness were deposited on p-type Si substrates by RF sputtering. Sputtered samples were annealed at 300-900°C for 30min in vacuum atmosphere. The results showed that, after low temperature annealing, a thin reaction layer of SiO_X was formed at the AZO/Si interface. After high temperature annealing, a Zn_2SiO4 phase was formed at the AZO/Si interface. The optical property of AZO after annealing showed more than 80% transmittance in a visible light range. Optical bandgap obtained by Tauc's method indicated the widening of the optical bandgap after annealing at 500°C. The electrical property results of AZO showed the lowest resistivity after annealing at 500 °C, while contact resistivity increased with increasing annealing temperature.

In Chapter 5, adhesion strength was measured. AZO films with 150nm thickness were deposited on p-type Si substrates by RF sputtering. Three types of AZO films were prepared; as-deposited, acid-etched, and post-deposition annealed. Then, Ag and Cu films with 100nm thickness were deposited on these AZO films by DC sputtering of Ag and Cu targets. Some of the metal/AZO samples were post-annealed at 300 °C for 30 min. The adhesion strength and electrical property of AZO/Si, Ag/AZO and Cu/AZO were evaluated. The results showed that the adhesion strength of AZO/Si was relatively strong in the as-deposited condition, however once interface reaction occurs between AZO/Si, the adhesion strength of AZO/Si was decreased.

Meanwhile, the adhesion strength of Ag/AZO and Cu/AZO was relatively poor in the as-deposited condition, and the surface roughening of AZO by annealing or etching was found to be effective in increasing the adhesion strength of metal/AZO. The post annealing of metal/AZO at 300°C for 30minutes also increased the adhesion strength of metal/AZO. The contact resistivity of Cu/AZO showed that the annealing of AZO lead to better contact resistivity and the etching of AZO was the more efficient way to improve the contact resistance.

The combined effect of the roughness and surface morphologies of AZO were the main reason for the better adhesion strength and contact resistivity. The larger contact area between the surface-treated AZO and the upper metal led to the increase in adhesion strengthand contact resistivity.

In Chapter 6, diffusion barrier property of AZO films was investigated between Cu and Si. AZO films with 10nm or 50nm thickness were deposited on p-type Si substrates. Then Cu films with 50nm thickness were deposited on the AZO films. The sputtered samples were annealed at 300-700°C for 30min in vacuum atmosphere. The results show that, at annealing temperature below 600°C, the structure of Cu/AZO/Si remained unchanged. However, Cu was agglomerated on AZO at 500°C and 600°C. The AZO layer was found to have enough barrier property to prevent Cu diffusion into Si. When the annealing temperature rose to 700°C, the Cu agglomerated dramatically on the AZO layer. And Cu began to diffuse into Si, and formed a Cu3Si phase in the Si substrate. It indicated that the barrier property of AZO at 700°C was poor, due to Cu diffusion into Si through the grain boundaries of AZO. The electrical property of Cu/AZO/Si after annealing was also investigated. The sample annealed at 300°C showed the best electrical property in all annealing conditions. This was due to the decrease of the AZO resistivity with increasing temperature. However, when annealing temperature was increased further, the interface reactant of SiOx formed between AZO and Si became thicker which block current flow, and leads to the increase of contact resistivity.

To conclude, a thin reaction layer was formed at the interface between AZO and Si. Despite the layer formation, AZO could sustain the thermal stability under practical production condition at 250°C for 30minutes, showing the good conducting property and transmittance. Under this annealing condition, the resistivity of AZO decreased from the as-deposited condition. Etching of AZO surface could improve the adhesion property of metal/AZO effectively. AZO has enough barrier property as a diffusion barrier layer between Cu and Si up to the annealing temperature of 600°C.

Therefore, these results indicate that the AZO is a suitable candidate as a TCO material for solar cells.

論文審査結果の要旨

本研究はヘテロ接合型太陽電池表面に形成される集電のための透明導電膜に関する研究である。

太陽電池は再生可能エネルギーとして注目されており、その普及拡大が望まれている。多くの種類の太陽電池がある中で、シリコンセルが全体の 8 割を占めており、最もポピュラーな太陽電池である。本研究はその中でも最高性能を有する HIT 型太陽電池に着目した。HIT 型太陽電池は集電用透明導電膜に ITO を用いており、高価な In を含む ITO を安価な材料で置き換えることが期待されている。Al をドープした ZnO(AZO)は安価であるとともに、光透過率や電気特性が ITO と同等であり、代替材料として多くの研究がされている。しかし、AZO を太陽電池に用いるためには、Cu 配線/AZO/Si の積層構造において界面反応挙動を理解するとともに、界面接触抵抗や界面密着強度を評価する必要がある。よって本研究の目的は、Si 基板上に成膜した AZO 薄膜の特性を調査した上で、界面反応とそれに伴う電気特性の変化および密着強度を評価し、さらに長期使用時の信頼性に関する知見を得ることとした。

AZO は RF スパッタ法で成膜し、400℃の成膜およびその後の熱処理によって良好な電気特性を得た。また紫外・可視光領域の透過率は ITO と同等の 90%以上であった。AZO/Si を加熱したところ、界面反応が確認できた。600℃以下においては AZO から Si によって還元され厚さが 2nm 以下の SiO2 層が形成された。700℃以上においては Zn_2SiO_4 層が形成され、900℃においては 20nm に成長した。また、界面層の形成と成長に伴って接触抵抗は上昇することが明らかになった。反応の温度依存性から算出した活性化エネルギーを利用して、JIS 規格による信頼性試験条件における界面層の厚さを見積もったところ、8nm の SiO_2 層が形成されることが予想された。このため、より熱的安定性に優れた透明導電膜の開発が必要であることが判明した。界面密着強度はスクラッチ法にて測定し、熱処理による界面反応によって剥離強度が 40mN へ上昇した。また、化学的に表面をエッチングすることで 55mN まで上昇した。これらの結果は界面粗さとの対応関係を見出すことができた。

AZO/Si 上に引き出し電極としての Cu 薄膜を形成して、熱処理による界面反応を調査した。その結果、500℃以下では Cu/AZO の反応は生じないが、700℃以上において Cu の凝集に続いて、Cu が AZO を貫通して Si と反応することが明らかになった。この結果より、AZO は 500℃以下では Cu と Si の拡散バリア層として機能することが判明した。

得られた結果は Cu/AZO/Si の界面反応に由来する性能と信頼性に関するデータを系統的かつ詳細に調査しており、HIT 型太陽電池の高性能化・信頼性化に向けて有用な情報となる。

よって、本論文は博士(工学)の学位論文として合格と認める。