Thin Solid Films 587 (2015) 156–159

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Effects of bath composition on the morphology of electroless-plated Cu electrodes for hetero-junctions with intrinsic thin layer solar cell

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ARTICLE INFO

Available online 27 February 2015

Keywords:
Electroless plating
Selective plating
Copper
Complexing agent
Surfactant
Heterostructure with intrinsic thin layer solar cell

ABSTRACT

The morphology of an electroless-plated Cu electrode was investigated as a function of bath composition. To enhance the selectivity of Cu electrode deposition on the surface of an indium tin oxide layer, a Ti/Cu multi-layer was deposited as a Cu electrode seed layer by physical vapor deposition, and then electroless plating was performed using various complexing agents and a surfactant. The degree of selectivity was effectively influenced by the type of complexing agent. The electroless plating solution containing N,N,N′,N′-tetrakis(2-hydroxypropyl)ethylenediamine (THPED) as complexing agent showed excellent selective growth of the Cu electrode as compared to the solution containing ethylenediaminetetraacetic acid. Even though THPED led to better selective growth of the electroless-plated Cu electrode, the aspect ratio of electrode lateral growth was about 2.7 times that of vertical growth. By adding a nonionic surfactant, the ratio between vertical growth rate and lateral growth rate was improved about 4.6 times. The Cu–THPED electroless plating with nonionic surfactant provided a drastic decrease in lateral growth rate, compared with the Cu–THPED electroless plating bath excluding nonionic surfactant. The Cu–THPED solution including nonionic surfactant is a promising composition of electroless plating solution for the clear selective plating of Cu electrodes on hetero-junctions with intrinsic thin layer solar cells.

1. Introduction

The photovoltaic market has grown tremendously during the past decade. Among various solar cell structures, the hetero-junctions with intrinsic thin layer (HIT) cell has been attracting a growing amount of attention due to its high conversion efficiency with simple cell structure [1,2].

Generally, the bus and finger electrodes of the HIT solar cell are made of resin-bonded silver paste by screen-printing process.

However, the efficiency of the HIT cell can be reduced by the wide width of the silver paste electrode [3]. Furthermore, the silver paste represents 25% of the total material costs for the solar cell, which leads to increased HIT cell manufacturing costs in the event of rising silver prices [4]. In an effort to increase the conversion efficiency by narrowing the width of the electrode, and reduce the manufacturing costs of the HIT cells, some studies have investigated methods of forming Cu electrodes using electro or electroless Cu plating processes [5,6]. It is already well known that Cu micro-electrodes formed using the electro- and electroless-plating copper process have very effectively increased efficiency and reduced manufacturing costs of some solar cells [5]. So far, however, there has been little study on electro- and electroless-plating of a Cu electrode for HIT cells [6]. Actually, it is difficult to selectively grow the Cu electrode in that application because the surface of the HIT cell is covered with indium tin oxide (ITO) as a conductive material. In this study, we investigated the effect of bath composition on the surface morphology of an electroless-plated Cu electrode for the HIT solar cell, considering the selectivity and plating rate.

2. Experimental details

To form a Cu electrode on the ITO surface via electroless plating process, a Ti/Cu multi-layer was deposited as a seed of the Cu electrode by physical vapor deposition (PVD). The width and thickness of the seed of the Cu electrode were 55.3 μm and 1.1 μm, respectively.

The HIT cell wafer was diced in a square shape of 2 cm × 2 cm for use as a substrate. To remove organic matter and debris from the substrate surface, it was cleaned by acetone, ethanol and deionized water for 10 min each using an ultrasonic cleaner and dried with N_2 gas. The solutions were made up of analytical grade chemicals from Sigma-Aldrich and deionized water treated by reverse osmosis and UV process.

In this study, Cu–ethylenediamine tetra acetic acid complex (Cu–EDTA) solution and Cu-N,N,N′,N′-tetrakis(2-hydroxypropyl)ethylenediamine complex (Cu–THPED) solution were used for the electroless plating bath. The Cu–EDTA bath was composed of 15 g/l $CuSO_4 \cdot 5H_2O$ as metal salt, 30 g/l Na_2EDTA as complexing agent,

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http://dx.doi.org/10.1016/j.tsf.2015.02.039
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0.02 g/l 2,2′-dipyridyl, 0.5 mg/l 2-mercaptobenzothiazole (2-MBT) as stabilizer, 20 ml/l 37% HCHO as reduction agent and KOH as pH adjusting agent. The pH of the solution was 12.5, and the temperature was maintained at 70 °C. The Cu–THPED bath was composed of 12.7 g/l $CuSO_4 \cdot 5H_2O$ as metal salt, 48.11 ml/l THPED as complexing agent, 0.2 g/l 2,2′-dipyridyl, 0.5 mg/l 2-MBT as stabilizer, 10 ml/l 37% HCHO as reduction agent and NaOH as pH adjustment. The pH of the solution was 13.2, and the temperature was maintained at 47 °C. To improve the selectivity and growth rate in the vertical direction of the Cu–THPED bath, 1 ml/l Triton X-100 (TX-100) diluted to 1.8% was used as nonionic surfactant.

The electroless Cu plating process was performed on the substrate in a 250 ml beaker in a thermostat at steady temperature. During the process, the substrates were placed in a vertical position and dipped in the Cu-complex electroless plating bath for 30 min. After electroless plating, the substrate was rinsed with DI water in an ultrasonic cleaner.

The morphology of the surface was observed by optical microscopy (OM, BX51M, Olympus) and the perpendicular thickness of cy (SEM, JSM-7001F, JEOL) with an accelerating voltage of 15 and 20 kV. A potentiostat (Versastat3, AMETEK) was used to evaluate the electrochemical reaction by linear sweep voltammetry (LSV) in the presence or absence of TX-100. The working electrode was the 2 cm × 2 cm Cu substrate with 1 cm^2 surface area, the counter electrode was a platinum mesh, and a Ag/AgCl electrode was used as a reference electrode, respectively. To remove Cu oxide from the working electrode, it was soaked in 10% sulfuric acid solution for 10 s.

Prior to each test, the electrodes were immersed in the electrolyte until open circuit potential was reached. Anodic LSV was carried out from −0.80 to −0.35 V at a scan rate of 50 mV/s in Cu–THPED bath, except for Cu metal ions, to figure out the behavior of HCHO-oxidation.

3. Results & discussion

3.1. Improvement of selectivity of electroless Cu plating

Fig. 1(a) and (b) are OM images of the surface of the HIT cell before and after electroless plating using the Cu–EDTA solution, respectively.

The dark blue area in Fig. 1(a) is an active area of the HIT cell covered by ITO and the bright yellow area is the Ti/Cu multi-layer electrode pattern sputtered by PVD. The non-selective electroless plating on the surface of the Cu electrode and ITO is shown in Fig. 1(b).

In order to determine the mechanism leading to such non-selective electroless Cu plating, we considered the reaction stages that occurred on the surface of the HIT cell as a function of electroless plating time. These were:

(1) Cu^{2+} reduction–HCHO oxidation at the surface of the Cu electrode in the initial stage;
(2) Decrease of Cu^{2+} concentration at the surface of the Cu electrode and movement of electrons to the outside of the electrode through the conductive ITO layer;
(3) Reduction of Cu^{2+} onto the ITO layer by combination with moved electrons.

Based on the above scenario, the weak binding strength between a Cu ion and complexing agent could elevate the degree of non-selective electroless Cu plating by accelerating the reduction of Cu ions onto the ITO layer. In the case of the Cu–EDTA bath, it is thought that Cu ions were readily reduced by electrons at the ITO surface owing to the weak binding strength of Cu^{2+}–EDTA, resulting in non-selective electroless Cu plating.

To investigate the effect of the binding strength of the complexing agent, EDTA was substituted with THPED as a complexing agent in the Cu electroless plating bath. As shown in Fig. 1(c), the selectivity of electroless-plated Cu electrode was certainly improved. The improved selectivity with Cu–THPED electroless plating is presumed to be due to the higher binding strength of Cu^{2+}–THPED, as compared to that of Cu^{2+}–EDTA.

That is, the combination of Cu ions with electrons can be inhibited by the strong binding strength of Cu^{2+}–THPED, resulting in the suppression of electroless Cu plating onto the ITO surface. However, after

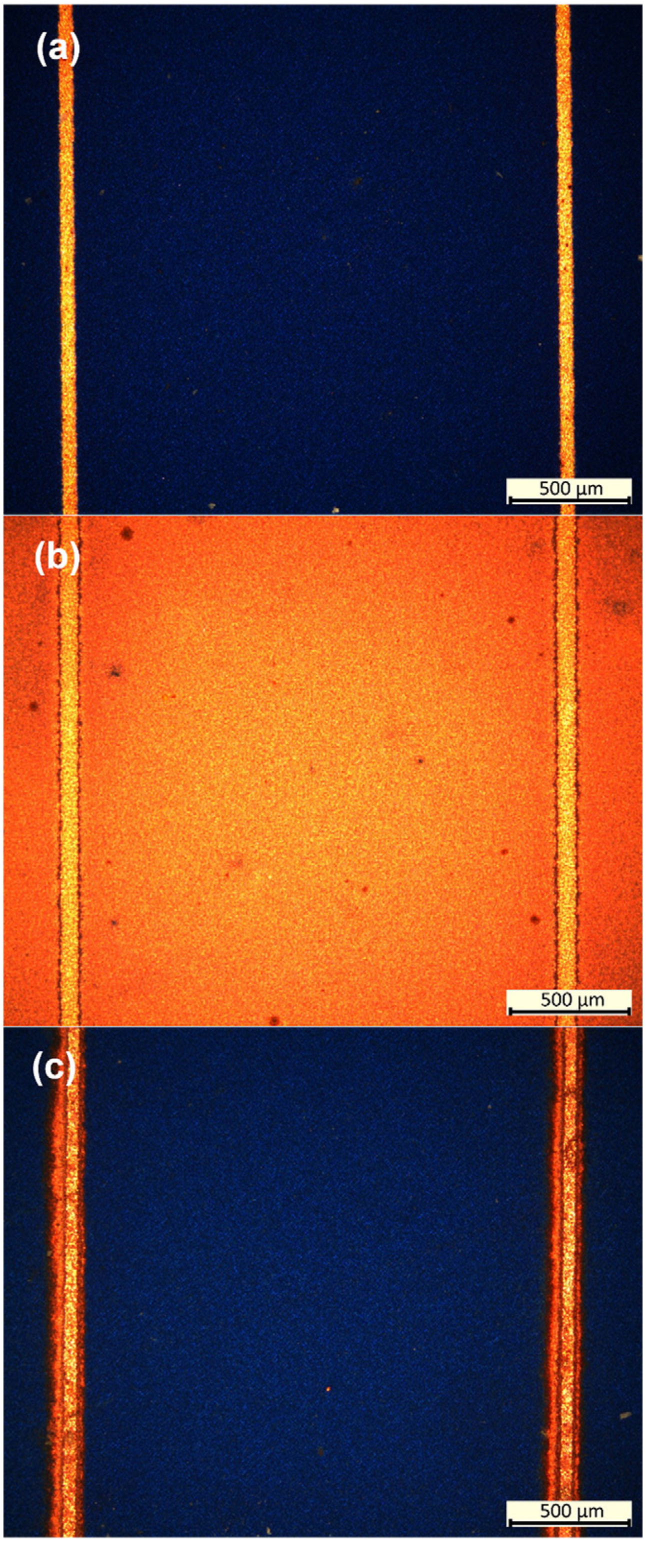

Fig. 1. OM Images of the HIT cell surface: (a) before the electroless plating; (b) after the electroless plating using Cu–EDTA solution; (c) after the electroless plating using Cu–THPED solution.