Copper Electrode on Flexible Substrate by Intense Pulsed Light Sintering of Microsized Copper Particles

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***Abstract*—Metal electrodes deposited in a grid pattern onto flexible polymer substrates have been shown to be a viable alternative to replace indium tin oxide (ITO) as the transparent anode for organic photovoltaics. copper may be a better alternative in terms of cost and stability for large area low-cost solar modules, specifically on roll-to-roll platforms. These customized electrode patterns can be fabricated from copper nanoparticles through various printing techniques applicable to solution phase processing. The Intense Pulsed Light (IPL) technique has been used to sinter copper nanoparticles (~100nm) to fabricate conductive copper electrodes on flexible polymer substrates. However, compared to nanosized (~100 nm) copper particles, microsized (~2 um) copper is much cheaper. In this work, microsized (~2 um) copper is used to produce high conductive copper inks. The conductivity of the print can be adjusted through the use of surfactant. IPL sintering was optimized to obtain high conductivity copper films. Several microscopic and electrical spectroscopic characterization techniques such as scanning electron microscopy (SEM), x-ray diffraction (XRD), 4-point probe resistivity measurements were employed to characterize the copper electrodes.**

Keywords—Microparticles, Copper, Intense Pulsed Light, Sintering, ITO-free, Solar Cells

I. Introduction

The front electrodes in organic photovoltaics (OPVs) and perovskite solar cells (PVSCs) need to be transparent and highly conductive in order to reduce the shadowing losses and lower the series resistance and hence to improve the power conversion efficiency (PCE) of the solar cell. As the most popular transparent electrode of OPVs and PVSCs, indium-tin-oxide (ITO) has good optical transmittance of 87% [1] in visible region and low sheet resistance of 25.82 Ω/sq [2]. However, the ITO is not ideal for low-cost, large scale and flexible solar cells due to its brittleness, increasing price and high temperature process condition [3, 4]. Thus, ITO-free solar cells have been studied to replace ITO by using other conductive layer [5-7]. Among these conductive materials, copper has been used because of its high conductivity and low price. The transparent copper layer includes electroplated thick copper grid [8], spray-coated copper nanowires [9], sputtered copper mesh [10] and thermal evaporated ultrathin (~10 nm) copper film [11]. However, these methods cannot be commercialized due to extra process steps such as photolithography [8, 10], annealing in hydrogen [9] and wet chemical etching [10].

To fabricate copper layer with low cost, customized electrode pattern can be fabricated by printing copper nanoparticles through several printing techniques, for example screen printing, gravure and inkjet printing. After that, the printed copper nanoparticle film needs to be sintered to be conductive. Intense Pulsed Light (IPL), also know as flash light sintering or photonic sintering, is low cost and high through-put technique which has been used in the printed electronics industry. During IPL process, the printed nanoparticle film is sintered under high-energy light in a very short time (in milliseconds) in the atmospheric condition and finally forms a conductive layer through both chemical reactions and solid state modifications. The IPL sintering nanosized copper particles (~100 nm) has been studied [12, 13] and the final copper films have conductivity comparable to that of bulk copper metal. However, microsized copper particles are cheaper than nanosized copper in the market and IPL sintering microsized copper has not been fully understood. In this work, microsized (~2um) copper particle films were fabricated on the flexible substate and sintered in the atmospheric condition through IPL process. The impact of Sodium Dodecyl Benzene Sulfonate (SDBS) on the film sheet resistance was studied and the function of SDBS was discussed.

II. Material and Methods

The copper inks were prepared by mixing microsized (~2 um) copper particles (3 g), Polyvinylpyrrolidone (0.3 g) in 1-methoxy-2-propanol (1.29ml) with different amounts of Sodium Dodecylbenzene Sulphonate (SDBS) (the surfactant), as shown in Table I.

TABLE I. Components of All Samples

Samples	SDBS(g)	Main Components
S1	0	Copper particles (3 g); Polyvinylpyrrolidone (0.3 g); 1-methoxy-2-propanol (1.29 ml);
S2	0.05	
S3	0.1	
S4	0.3	

The copper ink was spin-coated onto the ultra-thin (100 um) flexible glass and dried on the hot plate under 100 °C for 5 mins. After that, the samples were sintered under IPL (1.52 J/cm^2) with different numbers of pulses (6 pulses, 9 pulses, 12 pulses).

The sheet resistance of the copper films was measured using a four-point probe station (Signatone Corporation) with a power source (KEITHLEY 2401 SourceMeter). The film microstructure was investigated by scanning electron microscope (SEM) (FEI Nova600 FEG-SEM) and x-ray diffraction (XRD) (BRUKER Discovery D8 HR-XRD) was used to study the oxidation of the copper nanoparticles.

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III. Experimental Results

A. Electrical properties

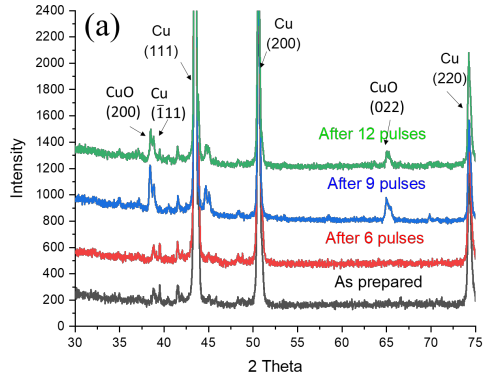
Table II shows the sheet resistance of all samples after different IPL pulses and all samples reached the lowest resistance after 9 pulses. Using high number of pulses for copper microparticles here is because the melting point of the particle is size effective [14] and micro copper particles have higher melting point than nanoparticles. The S1 (with no SDBS) reached the lowest sheet resistance of 0.28 Ω/sq and with more pulses (12 pulses), the films were overheated and turned to dark brown with higher sheet resistance. Compared with S1, after adding SDBS into the ink, the copper films become more conductive and S3 has the lowest sheet resistance of 0.055 Ω/sq which is about 5 times lower than that of S1. In addition, more SDBS in the ink made the film easier to be overheated and become darker after IPL. In this case, SDBS is the surfactant which can improve the thermal property of the ink and benefit the sintering of copper microparticles.

TABLE II. Sheet Resistance After IPL Sintering

Samples	Sheet Resistance (Ω/sq)		
	After 6 pulses	*After 9 pulses*	*After 12 pulses*
S1	41	0.28	0.33
S2	1.2	0.073	0.12
S3	0.18	0.055	0.069
S4	0.21	0.099	0.12

B. XRD analysis

To understand the IPL sintering copper microparticle film, XRD was used to characterize the components of the copper film before and after IPL process. According to other study [15], the copper nanoparticle is found to be covered by the copper oxide shell and the PVP in the ink acts as a reductant. During the IPL, the PVP can degrade to the intermediate alcohol and acid to react with copper oxide shell. Then these conductive copper particles were bonded together and form conductive film. As shown in Fig. 1(a), the as prepared S1 has mainly copper peaks [16] with no typical copper oxide. This indicates the copper oxide shell on microparticle is very thin. After 9 pulses sintering, the CuO (200) and (022) peaks [17] show up which means the copper film was oxidized and 12 pulses didn't further oxidize the copper particle but it overheated the film to be darker. In Fig. 1(b), all samples after 9 pulses sintering have the same peaks which means SDBS doesn't impact the chemical components of the copper particles.



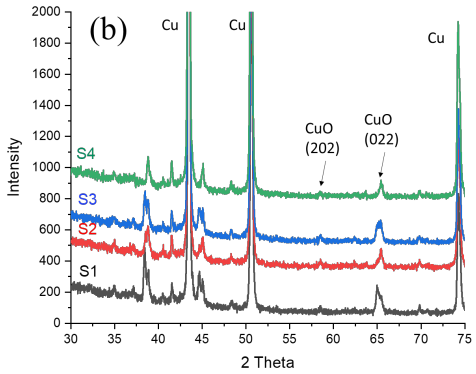


Fig. 1. X-ray diffracton patterns of (a) S1 before and after IPL sintering; (b) all samples after 9 pulses sintering.

C. Microstructural analysis

Fig. 2 shows the microstructure of all samples right after deposition and the film has uniform structure from the view of the cross-section and top surface. In Fig. 2(a), the prepared film has thickness around 10 um and the copper microparticles were fully covered by the PVP which insures PVP completely removing copper oxide during IPL. Fig. 2(b) shows the copper film has smooth surface which indicates the ink has desired viscosity and the surface tension.

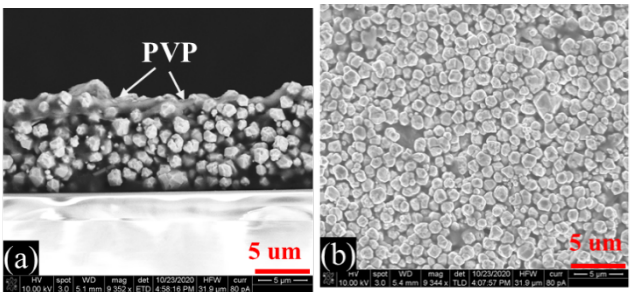


Fig. 2. SEM images of (a) the cross-section and (b) the top surface of the as prepared samples.

After IPL 9 pulses sintering, S1 and S3 became conductive, but the film morphology shows difference. According to the cross-section view in Fig. 3(a) and 3(d), S1 and S3 has similar film thickness but there was more PVP left in S1. The agglomerated PVP can better bind the microparticles together and make film more smooth in Fig. 3(b) than that in Fig. 3(e). However, the remaining PVP in S1 indicates the microparticles underneath the surface were not completely sintered and due to the nonconductive nature of PVP, S1 has higher sheet resistance than S3. Based on Fig. 3(c) and 3(f), the microparticle bonds in both S1 and S3 are weak compared to the nanoparticle bonds [18]. Thus, the rough surface of S3 in Fig. 3(e) is caused by the larger explosive force of vapor from PVP. In another word, S3 has more PVP degraded during the IPL compared with S1. This means SDBS can cause PVP absorb more energy under the IPL and better sinter the microparticles with less PVP left in the film.

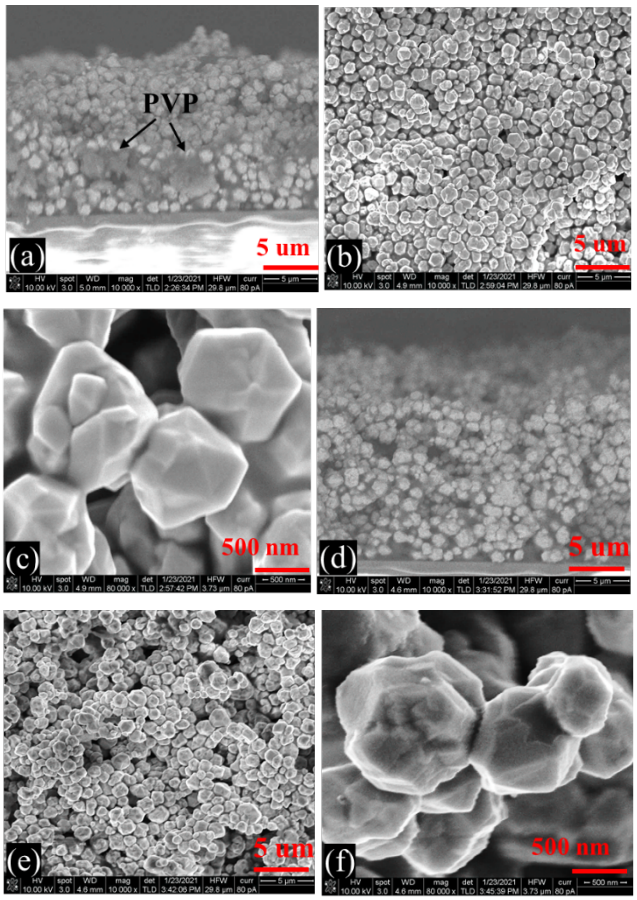


Fig. 3. SEM images of S1 (a)-(c) and S3 (d)-(f) from the cross-section view (a)&(d), top view (b)&(e) and particle bonds (c)&(f).

D. UV-vis analysis

The impact of the SDBS on the optical property of the PVP was studied as shown in Fig. 4. The PVP was prepared by mixing Polyvinylpyrrolidone (0.3 g) in 1-methoxy-2-propanol (1.29ml) with different amounts of SDBS followed by spin coating on the glass and drying under 100 ºC for 5 mins. It can be found in Fig 4(a) that PVP and SDBS doesn't have absorption peak over 300 nm. In Fig 4(b), with increasing the amount of SDBS, the PVP absorbs more light around 230 nm with a red shift due to the absorbance of SDBS at 224nm which refers to benzene ring [19]. The absorbance at 260 nm is increased with more concentrated SDBS in PVP film. Due to the enhanced absorption of PVP in UV region, more PVP deep inside the film was removed which matches with UV decomposing PVP [20]. At the same time, more copper particles can be sintered at the same time with PVP. Hence, the metal film has lower sheet resistance. However, too much SDBS will cause larger explosive force of vapor from PVP and remove more copper particles leading to higher resistance.

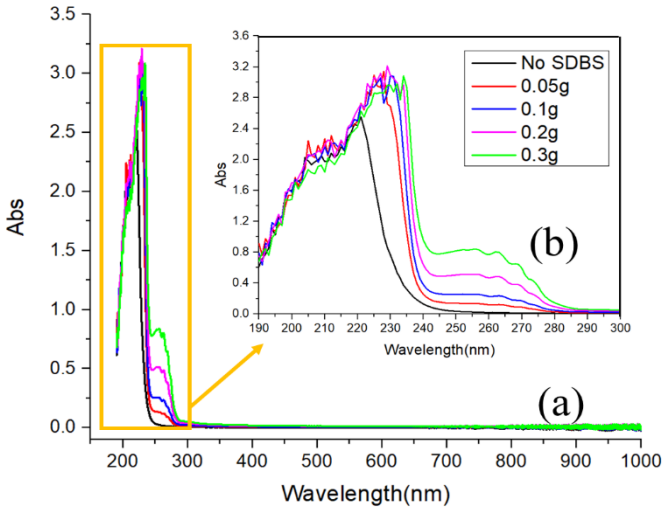


Fig. 4. (a) UV-vis of PVP film with different amount of SDBS with (b) spectrum in UV range.

IV. Summary

The copper microparticle film was sintering through IPL process and the impact of SDBS on the film conductivity was studied. Because the microparticles have higher melting point than nanoparticles, it requires 9 pulses to completely sinter the microparticle film and to reach the lowest sheet resistance. After adding SDBS, the sintered film is more conductive but easier to be overheated. According to the XRD analysis, the copper microparticle has very thin copper oxide shell and it became further oxidized under the optimized sintering condition (9 pulses). More pulses will overheat the film and cause higher sheet resistance. From SEM images, particle bonds were formed in both S1 and S3 but S3 has rougher surface than S1 because less PVP remained in S3. Based on the UV-vis analysis, SDBS has the function of modifying the optical property of the PVP and causes PVP absorbing more UV light. The absorbed UV light can help sinter the PVP and copper particles below the surface causing less PVP remaining and lower sheet resistance. In this case, microsized copper particles can achieve low resistance through IPL process with proper surfactants.

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