



Transparent conductive polymers for laminated multi-wire metallization of bifacial concentrator crystalline silicon solar cells with TCO layers



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ABSTRACT

Replacing expensive silver with inexpensive copper for the metallization of silicon wafer solar cells can lead to substantial reductions in material costs associated with cell production. A promising approach is the use of multi-wire design. This technology uses many wires in the place of busbars, and the copper wires are “soldered” during the low-temperature lamination process to the fingers (printed or plated) or to the transparent conductive oxide (TCO) layer, e.g. in the case of the a-Si:H/c-Si heterojunction cells. Here we describe a solar cell design in which wires are attached to TCO layers using transparent conductive polymer (TCP) films. To this end, we have synthesized a number of thermoplastics, poly(arylene ether ketone) copolymers (co-PAEKs), containing phthalide in their main chain. The fraction of phthalide-containing units in the copolymers was $p=3, 5, 15, \text{ and } 50 \text{ mol\%}$. With increasing p , the peak strain temperature of the co-PAEKs rises from 205 to 290 °C and their optical band gap and refractive index increase from 3.12 to 3.15 eV and from 1.6 to 1.614, respectively. The copolymers have a negligible absorption coefficient in the wavelength range 400–1100 nm. When exposed to an excess pressure of 1 atm or above, co-PAEK films less than 30 μm in thickness undergo a transition from a dielectric to a conductive state. The resistivity (ρ_C) of wire/TCP/TCO (ITO=In₂O₃:Sn and IFO=In₂O₃:F) contacts ranges from 0.37 to 1.43 mΩ cm². The polymer with the highest phthalide content ($p=50 \text{ mol\%}$) has the lowest ρ_C . The average work of adhesion per unit area determined by pulling off the wires from the polymer surface depends on both the phthalide content of the co-PAEKs and their reduced viscosity, ranging from 14.3 to 43.5 N/cm. The highest value was obtained for the co-PAEK with $p=50 \text{ mol\%}$. We have fabricated low-concentration bifacial IFO/(n⁺pp⁺)Cz-Si/ITO solar cells with a wire contact grid attached to IFO and ITO using a co-PAEK film. The efficiency of the best cell under 1× to 7× front/rear illumination was determined to be 18.3–18.9%/15.0–15.6%.

1. Introduction

A key direction in addressing the major challenge of solar power conversion—photovoltaic energy cost reduction—is the development of an economically attractive process for producing a current-collecting system [1]. For diffused-junction wafer-based crystalline silicon (c-Si) solar cells, which currently dominate in the industry, high temperature (800–900°C) screen printing of silver and aluminum pastes is the standard metallization process. Research effort focuses on both reducing silver consumption and replacing silver by copper [2,3].

The use of transparent conductive oxide (TCO) layers in solar cells, e.g. in those based on TCO/a-Si:H/c-Si structures [1,4], containing amorphous silicon (a-Si:H) layers, on TCO/(n⁺pp⁺)c-Si or TCO/(p⁺nn⁺)c-Si structures [5–7], with a p–n junction, and on TCO/(c-Si)

heterojunctions [8,9], imposes certain limitations on the metallization temperature because of the possible degradation of the electrical and optical properties of the TCO and a-Si:H layers and interfaces [10–12]. At present, silicon solar cells containing TCO layers are metallized using silver pastes with low curing temperatures (under 250 °C) [11,13,14]. Polymer materials and low-temperature solders are used as components of the pastes that ensure adhesion to the TCO surface. However, the resistivity of even the best low-temperature pastes is three times that of high-temperature pastes [15]. Because of this, to avoid an increase in resistive losses, silver paste consumption should be increased three times, which will lead to an undesirable increase in silver consumption. It should be emphasized that silver pastes are among the most expensive materials (second only to silicon wafers) in the manufacture of solar cells [1,16]. Several approaches for reducing

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silver consumption in the metallization of solar cells with TCO layers are under development. One of them is to use copper pastes [17]. The problem with this approach is that one should prevent copper oxidation and copper diffusion into silicon. Moreover, the resistivity of such pastes is even higher than that of the silver pastes. Nevertheless, copper pastes can be successfully used for producing busbars [18]. Another approach is based on the electroplating of a Ni/Cu stack. It requires no high temperatures and employs cheap materials, but electroplated contacts have poor adhesion to TCOs and, moreover, a rather complex and expensive process is needed to produce them [19]. Finally, in recent years ever increasing attention has been paid to the multi-wire approach, which uses many solder-coated wires instead of a few (usually three) busbars, and the wires are "soldered" to printed or electroplated fingers during the lamination process. The multi-wire approach allows silver consumption to be reduced owing to the less stringent requirements for the longitudinal resistance of the fingers [3,20,21]. This technology is used by Meyer Burger AG (Smart Wire Connection Technology) [22,23], and Schmid Group (multi-busbar design) [24]. Their designs allow silver consumption to be reduced by up to ~80%.

Yet another approach for forming silver-free contacts to solar cells with TCO layers was proposed previously by our group: laminated grid cell (LGCell) design. The current-collecting grid in the LGCell design also consists of an array of solder-coated wires, but the wires form direct contact to the TCO, without any printed or electroplated fingers, and are secured to the TCO layer by lamination film [25,26]. The LGCell design ensures low metallization resistance and low shading losses, so it can be used e.g. in low-concentration solar cells [26,27]. It is worth noting however that the solder the wire is coated with has poor adhesion to the TCO surface, so the contact system may be damaged in the solar module encapsulation step.

To ensure thermal stability of the wire/polymer/TCO system up to temperatures at which solar cells are encapsulated to form a module (~140 °C), we proposed attaching wires to the TCO surface using transparent conductive polymers (TCPs), both thermoplastic and thermosetting [28,29]. Therefore, thermoplastic TCPs should have softening onset temperatures above 140 °C.

In this paper, we report the synthesis and properties of a number of thermoplastics, poly(arylene ether ketone) copolymers (co-PAEKs), differing in the percentage of phthalide-containing units in their main chain: $p=3, 5, 15,$ and 50 mol%. These TCPs are electroactive non-conjugated polymers: when exposed to a uniaxial pressure above 0.4 atm, films of these polymers less than 30 μm in thickness undergo a transition from a dielectric to an anisotropic, highly conductive state in the compression direction (with a resistivity on the order of $10^{-5} \Omega \text{ cm}$), while retaining chemical and physical properties typical of plastics [30,31]. In addition, they are transparent in the range $\lambda=400\text{--}1200$ nm. It is worth noting that Salazkin et al. [32] were the first to synthesize and investigate polymers exhibiting the electron switching effect. The best studied electroactive polymers, polyarylene-naphthalides, have recently been the subject of ever increasing attention owing to their unusual electrical properties [32–34]. Two inter-related factors determine their unusual properties. One of them is their unique film-forming properties, which allow uniform, continuous films as thin as a monolayer to be produced on solid surfaces. The other factor is the presence of phthalide in the main chains of the copolymers. Its interaction with an excess charge causes the electronic states of the macromolecule to redistribute so that a band responsible for carrier transport is formed near the Fermi level of the polymer. Varying the phthalide content of co-PAEKs, one can control not only the electrical properties of these TCPs but also their thermomechanical properties. Present work is concerned with how the chemical composition of the co-PAEKs influences their optical and thermomechanical properties (softening onset temperature), and the contact resistivity of wire/polymer/TCO structures is determined by transmission line model (TLM) measurements. We produced bifacial low-concentration

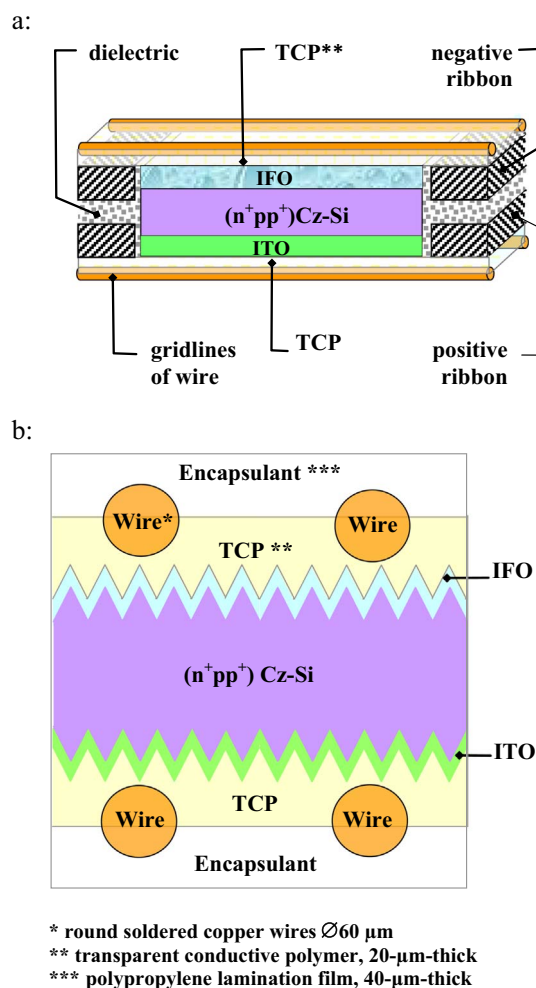


Fig. 1. Schematic of a bifacial TCP-containing LGCell: sections (a) along and (b) across the wires. The cell in picture a) is not encapsulated.

LGCell devices based on an IFO/(n^+pp^+)Cz-Si/ITO structure (where Cz-Si=Czochralski silicon, ITO= $\text{In}_2\text{O}_3:\text{Sn}$, and IFO= $\text{In}_2\text{O}_3:\text{F}$), using co-PAEK films in the contact system. The bifacial LGCell design is schematized in Fig. 1. A TCP film ~20 μm in thickness covers the entire solar cell surface to ensure electrical contact between the current-collecting wire grid and the TCO-coated silicon solar cell surface. The TCP is also used to attach wires to busbars outside the solar cell (Fig. 1a). A similar contact is made on the backside of the bifacial LGCell.

2. Experimental

2.1. Polymers

Fig. 2 shows the chemical structure of the synthesized co-PAEKs, which have different phthalide to isopropylidene ratios ($p:q$). The content of phthalide-containing units, p , was 3, 5, 15, and 50 mol%. Hereafter, these polymers will be referred to as P3, P5, P15, and P50, respectively.

The co-PAEKs were synthesized through polycondensation using nucleophilic substitution for an activated halogen in an aryl halide, by reacting 4,4'-difluorobenzophenone with dipotassium bisphenolates, similarly to the preparation of homopolymers previously reported [35]. The co-PAEK synthesis procedure was described in detail elsewhere [36]. Reduced viscosity η_{red} was determined in chloroform at 25 °C and a polymer concentration of 0.5 g for 100 ml of a solvent,

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