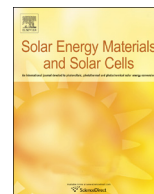




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Quaternary phosphonium salts as cationic selective dispersants in silver conductive pastes for photovoltaic applications



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ABSTRACT

Over a dozen novel cationic phosphonium dispersants were used in preparation of conductive silver pastes for photovoltaic applications. We investigated the relationship between the structures of phosphonium compounds and the efficiency of p-type silicon PV cells and the phosphorus interaction with the wafer, frit, and silver particles in the paste. Three dispersants were found to be the most beneficial with increases in the cell efficiencies of 0.1–0.3% on poly-crystalline and mono-crystalline Si cells. All of them have long chain substituents at phosphonium function and weakly coordinating anions. Better dispersion of metal oxide particles, which are making the frit, was seen when these phosphonium dispersants are present. Laser ablation – ICP-MS was used to measure the phosphorus profile, and was able to detect phosphorus within silver particles and the silicon substrate indicating the possibility of self-doping. Additionally, the transmission line method (TLM) was applied to quantify the contact resistivity.

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1. Introduction

Photovoltaic technology is becoming one of the most dynamic contributors to energy sector of the economy. The legitimate promise of decreasing dependency on oil and natural gas has found support among many governments around the world. As a result, different alternative photoabsorber materials are on the market, e.g., crystalline silicon, germanium, and cadmium telluride; or are making their way to the market, e.g. $\text{CuIn}_x\text{Ga}_{(1-x)}\text{Se}_2$ (CIGS) and $\text{Cu}_2\text{ZnSnSe}_4$ (CZTS). The conductive electrode materials used for photovoltaic applications are not that diverse. Metallic silver for the front of the cell and metallic aluminum for back side of the cells are predominant materials for crystalline silicon, CIGS and CZTS. The fact that silver has the highest electrical conductivity and prices below gold will keep silver electrodes on the market for a long time to come. Screen printing remains one of the most common ways to apply silver electrodes to cells. Silver pastes for screen printing are very dense dispersions with solids up to 90% by weight solids and viscosities in the range from 200 to 400 Pa/s. This is why surfactants and dispersants play an important role in metallization paste production. Anionic, neutral and cationic surfactants have been used in metallization pastes [1]. Ammonium-based cationic surfactants have typically been used to disperse silver particles and frit particles in an organic vehicle [2]. Phosphorus is a key element in

the making silicon-based PV cells since it is the dopant used in the emitter of p-type silicon cells. So, the application of the phosphorus-based surfactants has been proposed to contribute to a self-doping mechanism of p-type silicon PV cells. Anionic phosphorus-containing surfactants with phosphate groups were reportedly used for that purpose [3]. Here, we present the novel application of cationic phosphorus dispersants for that purpose.

Fourteen phosphonium derivatives were tested in our experiments with silver pastes. The effectiveness of different counteranions in the phosphonium salt, for example, chlorides, bromides, dicyanamide, deconoate, sulfate, methanesulfonate, bis(trifluoromethane-sulfonyl)amide, phosphinate, phosphorodithiate and phosphate were scouted. Variations in the length of alkyl substituents at the phosphonium moiety were evaluated as well. Fig. 1 shows the structures of phosphonium derivatives tested in the preparation of the silver metallization pastes.

Because PV cell performance depends on the starting materials as well as the silver paste, monocrystalline and polycrystalline wafers from several manufacturers were included in this evaluation.

2. Experimental section

2.1. Reagents and materials

Trihexyl(tetradecyl)phosphonium chloride (**1**), trihexyl(tetradecyl)phosphonium bromide (**2**), trihexyl(tetradecyl)phosphonium

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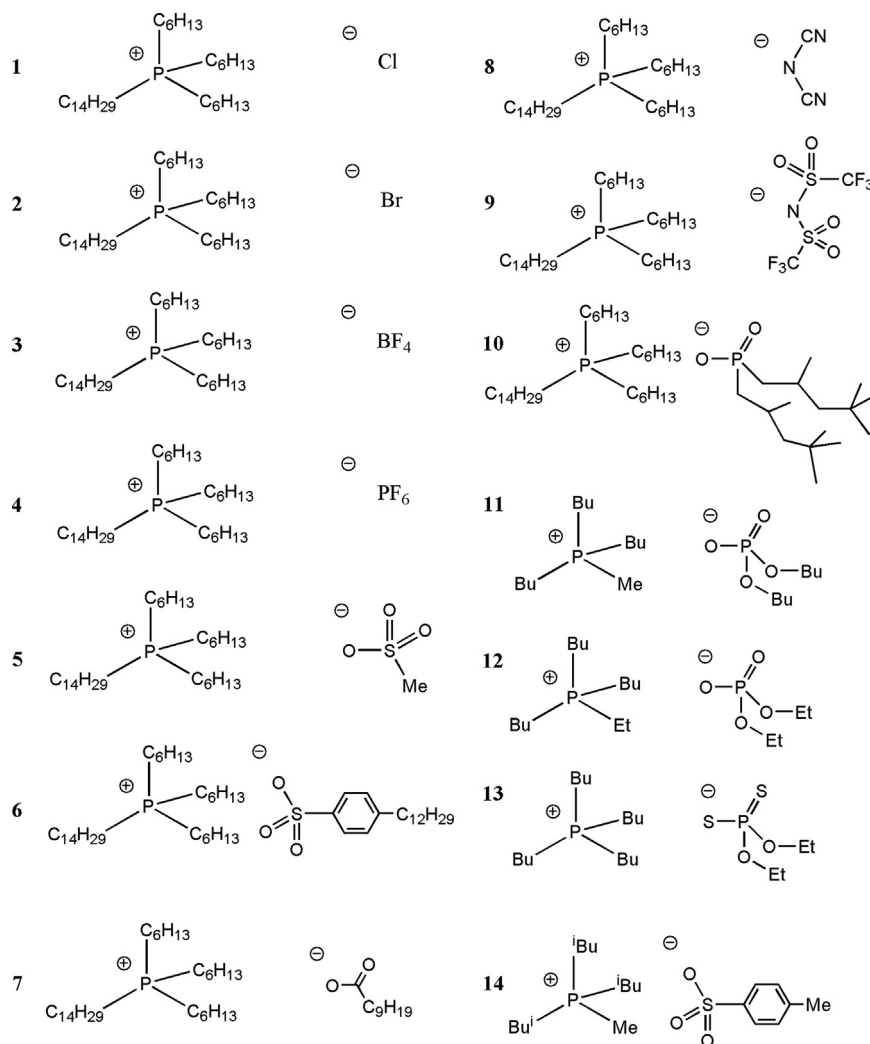


Fig. 1. List of phosphonium derivatives used as dispersants in silver paste preparation.

tetrafluoroborate (**3**), trihexyl(tetradecyl)phosphonium hexafluorophosphate (**4**), trihexyl(tetradecyl)phosphonium metanesulfonate (**5**), trihexyl(tetradecyl)phosphonium dodecylbenzenesulfonate (**6**), trihexyl(tetradecyl)phosphonium decanoate (**7**), trihexyl(tetradecyl)phosphonium dicyanamide (**8**), trihexyl(tetradecyl)phosphonium bis(trifluoromethanesulfonyl)amide (**9**), trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (**10**), tributylmethylphosphonium dibutyl phosphate (**11**), tributylethylphosphonium diethyl phosphate (**12**), triisobutylmethylphosphonium tosylate (**14**) were purchased from Aldrich, Strem or directly from Cytec Inc. Tetrabutylphosphonium diethyl dithiophosphate (**13**) was purchased from Waco Chemicals. The organic medium consists of different blends of ethyl cellulose dispersed in an organic solvent. A rheological additive is also added into organic vehicle for proper printability. Inorganic ingredients, such as silver powders and metal oxide-containing frits are commercially available from several suppliers.

2.2. General paste preparation

Paste preparations were, in general, accomplished with the following procedure: the appropriate amounts of solvent, medium, surfactant and other constituents were weighed then mixed in a mixing can for 15 min, then metal oxide-containing frit was added and the product was mixed for another 15 min. The frit used in the following examples was milled to a D_{50} of 0.5–0.7 μm prior to use. Since Ag is the major part of the solids of the present work, it was

added incrementally to ensure better wetting. Thinky mixer (Thinky Corporation) was used for mixing. When mixed well, the paste was repeatedly passed through a 3-roll mill at progressively increasing pressures from 0 to 100 psi. The gap of the rolls was adjusted to 25 μm . The degree of dispersion was measured by fineness of grind (FOG). The FOG values were from 6/4 μm to 12/6 μm for our pastes.

Detailed preparation of a 50 g samples of silver pastes with 2.5% trihexyl(tetradecyl)phosphonium bis(trifluoromethanesulfonyl)amide (**9**) and with 2.5% trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (**10**) are presented in Table 1.

2.3. Screen-printing conditions

The pastes were screen-printed on 1 × 1 in., 200 μm thick, 65 Ω/sq mono or polycrystalline silicon wafers. The efficiencies of cells made on 1 × 1 in. wafers are substantially smaller than those on 6 × 6 in. or 5 × 5 in. wafers. The screen-printed pattern was 11 fingers with a busbar, as shown in Fig. 2.

Commercially available silver paste PV159 (DuPont) was used as a standard. Aluminum paste PV 381 (DuPont) was used to print a backside electrode. The screen for printing the back-side was 230 mesh, 1.4 mil wire, and 0.4 mil emulsion. The screen for printing the Ag front-side was 325 mesh, 0.9 mil wire, 1 mil emulsion, 100 μm -line width. Several firing programs were used starting at 810 and finishing

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