Ceramic Enamels as New Back Contacts for Cu (In, Ga) Se₂-Based Photovoltaic Tile

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In this work, we investigated the properties of silver and gold enamels as potential back contacts for Cu (In, Ga) Se₂ (CIGS) solar cells. The enamels were deposited on ceramic tiles by nonvacuum printing techniques. Thus, we are proposing a development of integrated photovoltaic tile for the first time. We also explained the CIGS synthesis procedure using coprecipitation of selenite precursors. To deposit the precursor powders on the substrate, a doctor blade method is applied. The interface morphology between ceramic tile, back contact, and CIGS absorber was studied as a critical factor for the final solar cell performance. The thermal treatment effect on the back contact properties was also reported. Excellent compatibility between CIGS and gold layer was observed, keeping thickness and chemical composition adequate for photovoltaic applications. The band gap energy confirms assembly effectiveness. Unsatisfied results of silver diffusion toward CIGS absorber were obtained when silver enamels were used.

Introduction

Thin-film technology is a desired alternative for preparing photovoltaic devices because of an enormous saving of costly materials and simplification of the manufacturing process. The low-cost potential of this technology is rooted by means of cheaper substrate applications, effective uses of raw materials, and thinner coatings (ranging from 1.5 to 3 μm).¹,² In this sense, ceramic tiles emerge as good alternatives for substrate by reducing production costs and giving benefits to the final products. An advantage is a possibility to use higher temperature treatments, keeping intact material thermal stability. The photovoltaic (PV) incorporation in building constructions as an energy source by replacing of conventional building materials (as roof, skylights, or facades) makes them very attractive for so-called building-integrated photovoltaics (BIPV).³,⁴ In addition, these systems can provide large areas of photovoltaic modules based on diverse absorbers.

Cu (In, Ga) Se₂ (CIGS) is an attractive absorber for thin-film solar cells due to its unique optical and electrical properties.⁵–⁷ CIGS technology has recorded 21.7% of efficiencies.⁸ The typical CIGS solar cell is constituted for soda-lime glass substrate (3 mm), sputtered molybdenum back contact (800 nm), CIGS absorber layer (2 μm), chemical bath deposited CdS buffer layer (10–60 nm), sputtered zinc oxide (i:ZnO), and/or indium tin oxide (ITO) as window layer.⁹ The use of vacuum-based technique for thin-film deposition is a main handicap of this technology.¹⁰,¹¹ Covering at room temperature and atmospheric pressures stand out as an attractive alternative for the absorber layers.¹²–¹⁷ Methods as doctor blade, spin coating, and dip coating are very suitable for that purpose, being cost-effective ways of preparation. In this connection, the doctor blade technique is very desirable from an industrial point of view for large-scale production due to its simplicity and availability at many factories (e.g., ceramic tile industrial units).¹⁰,¹⁸ The doctor blade, also known as tape casting, is a processing method for producing of thin films on large area surfaces with no waste of materials and good layer uniformity. Commonly, this method involves spreading through a moving blade onto a stationary substrate. There are three different type of doctor blade coating devices in use: a knife, a rectangular frame, and a spiral film applicator.¹⁹ The gap size of the blade governs the layer thickness. The micrometric precision of blade regulation is the main inconvenient of this way of deposition that leads difficult precise depth control. However, controlling coating parameters that influence to the film formation as surface energy of the substrate, surface tension of the fluid, coating or blade speed, fluid viscosity, density, and surface temperatures could solve this problem.²⁰,²¹

The soda-lime glass is probably the most used substrate in CIGS solar cell.²² Polymers and metals are also investigated as alternative options.²³–²⁶ Polymers have appropriate chemical inertness and do not react with selenium during the thermal treatment.²⁵ In addition, these materials have a smoother surface and humidity
barrier. However, they have low thermal stability to withstand thermal selenization treatment.

In contrast, metals have better thermal stability than polymers, but a barrier layer is required to block impurities that can diffuse toward the absorber layer. Concerning these drawbacks, the ceramics are good alternative substrates. The principal selection criteria that ceramics must fulfill are the following: compatible thermal expansion coefficient (CTE) (~ 7.10^-5 K^-1), excellent thermal (T > 600°C) and chemical resistivity, and being suitable for industrial uses in terms of costs and facilities. The CTE of ceramics is similar to the CTE of CIGS (8–11.10^-5 K^-1) and is relatively cheap product. Thus, ceramic tiles for substrates offer new possibilities for solar cells and its integration in urban areas (BIPV).

Commonly, the back contact layer is made of metal. It fabrication is well-studied part of materials engineering field. The main requirements for a good back contact for CIGS solar cells are as follows: inertness, smooth surface, good electrical properties (low contact resistance), good thermal stability, and cost, and it should act as diffusion barrier. The surface morphology plays a key role in the final electrical properties.

The back contact executed as a barrier acts as impurities diffusion membrane between the substrate and the absorber. Variety of metal/CIGS contacts have been investigated, including (Cu, Ni, Al, Mo, and Pt), (Ag), (Au), and others (W, Cr, Ta, Nb, V, Ti, and Mn) with limited success. The most applied metal is molybdenum (Mo). Despite of that, Mo deposition also presents certain problems related to bad substrate adhesion and fast metal oxidation. The back contacts used for high-efficiency devices are typically deposited by direct current (dc) sputtering, evaporation, or chemical vapor deposition (CVD) that increase the final value of the cell.

Although CIGS semiconductor has been studied for several decades, rather limited information has been reported in literature on metal morphology effects on the back contact resistance.

The study reports a development of new back contacts for CIGS solar cells. Substrate made by common porcelain stoneware ceramic tile is used. The tile was previously covered with industrial glazes containing gold or silver in its compositions. The glaze, situated between the CIGS absorber and the substrate, provides chemical stability, inertness, and roughness reduction. The glass nature of the enamels simulates flat surface with no porosity. The metal (gold or silver) content allows it to operate as a metal back contact. Nonvacuum, solution-based, and large-scale way of deposition, called ink printing, of the enamels for reducing materials and costs is suggested. In addition, simple way of preparation using coprecipitation route for the CIGS absorber is also reported. The developed powders were deposited on the substrate by doctor blade technique. The morphological properties in the interface ceramic tile/back contact/CIGS were investigated as crucial aspect for the final solar cell performance. Band gap energy was measured for the optimal sample testing the assembly effectiveness.

![Fig. 1. Schematic layout of a Cu (In, Ga) Se_2-based photovoltaic ceramic tile.](https://www.ceramics.org/ACT)

![Fig. 2. Surface morphology of Au thin film: (a) atomic-force microscope (AFM) surface image; (b) scanning electron microscopy (SEM) cross-section micrograph of Au layer; and (c) SEM micrograph of Au surface.](https://www.ceramics.org/ACT)
Experimental Details

Porcelain stoneware substrates (5 mm thickness) were made by industrial method of preparation using kaolinitic clay, feldspar, and feldspathic sand. The pastes (with average chemical composition (oxide wt%): 60–70 SiO₂, 18–20 Al₂O₃, 1.5–3 K₂O, 3.5–4.5 Na₂O, and 1–2 others oxides) were prepared by pressing and further sintering in a conventional kiln.

Industrial frit developed for the enamel applied in the solar cell contains the following average composition (oxide wt%): 55–65 SiO₂, 10–30 Al₂O₃, 0.5–5 Na₂O–K₂O, 13–17 MgO–CaO, and 10–20 others. The frits were applied to ensure low porosity and impermeability and to provide chemical stability and roughness reduction simulating thereby glass surface.

The gold dye over the frit was deposited by ink-jet printing in nonvacuum conditions for obtaining gold conductive enamel with a thickness ~200 nm. The same procedure was applied for the silver enamel (~2.50 μm thickness), but the silver dye was deposited by screen-printing technique. These coating methodologies, ink-jet and screen printing, were selected to determine their effectiveness. They achieved different layer depths and morphologies that may influence to the device properties. In Fig. 1, schematic design of the photovoltaic ceramic tile is shown.

CuIn₀.₇Ga₀.₃Se₂ solid solution was synthesized using coprecipitation route of metal selenite precursors, keeping atomic ratio of Cu/(In + Ga) = 0.92 and Ga/(In + Ga) = 0.3.¹⁴ The resulting CIGS powder was further mixed with triethanolamine (TEA, 99%, Riedel-de Haën, Seelze, Germany) and ethanol (C₂H₅OH, 99.9%, Sharlau, Barcelona, Spain) to form slurry that was deposited on ceramic substrate by manual knife doctor blade method. The slurry viscosity and the blade gap mainly govern the thickness precision.

The obtained layer was preheated on a hot plate at 400°C for 2 min to remove partially the solvent and to encourage further precursor decomposition. Finally, the CIGS films were selenized under reducing atmosphere (5% H₂/95% N₂) in a tubular furnace. The applied thermal cycle corresponds to heating velocity rate of 20°C/min up to maximum temperature of: 200°C (sample A); 350°C (sample B); 450°C (sample C); 500°C (sample D); and 550°C (sample E). Free cooling and no soaking time were applied.

Crystal structure of powders and films was monitored by X-ray diffraction (XRD) using a D4 Endeavor, Bruker-AXS equipped with a Cu Kα radiation source. Data were collected by step scanning from 10° to 80° with step size of 0.05° and 1 s counting time per step.

The particle sizes were quantitatively evaluated from the XRD data using the Debye–Scherrer equation,⁴³

\[ D = \frac{k \lambda}{\beta \cos \theta} \]  (1)

where k is Scherrer constant (0.89), λ the X-ray wavelength (0.15405 nm), β the peak width of half-maximum, and θ is the Bragg diffraction angle.

Scanning electron microscopy (SEM) model JEOL 7001F attached with an energy-dispersive X-ray analysis (EDX) was employed to study the morphology and elemental composition of the films. The layer thickness was determined from cross-section micrographs. The glaze surfaces were studied by atomic-force microscope (AFM) with a JSPM-5200 JEOL scanning probe microscope operating in contact approach. Adhesion between back

![Fig. 3. X-ray diffraction pattern of Au layer before Cu (In, Ga) Se₂ deposition.](image)

![Fig. 4. X-ray diffraction of Cu (In, Ga) Se₂ films after thermal treatment at: (a) 200°C, (b) 350°C, (c) 450°C, (d) 500°C, and (e) 550°C.](image)
contact layers and support was measured using laboratory test method by applying and removing tape and scratching of the surface. This method is used to establish whether the adhesion of a coating to a substrate is at a generally adequate level. The film’s electrical resistance was measured using a digital multimeter (Volt–Ohm meter).

Optical properties and band gap energy of the CIGS layer were conducted by UV–Vis–NIR spectroscopy in the wavelength range 200–1200 nm (step size 1 nm) using Cary 500 Scan Varian spectrophotometer (Agilent Technologies Spain S.L., Madrid, Spain). The absorption spectra were obtained applying BaSO4 integrating sphere as a white reference material.

Results and Discussion

Physical characteristics of the ceramic body were analyzed. The obtained tile density was 2.056 g/cm³ after thermal treatment at 1200°C (data not shown). The vitrification plot displayed linear contraction of 7.56% and water absorption of 0.98% at 1165°C. These values remained constant even at 1190°C, where the water absorption decreases up to 0% (data not shown).

Figure 2(a) displays AFM images of the Au enamel layer. Rather smooth and regular surface of polycrystalline gold enamel is observed. The average roughness is about 3 nm, very suitable for layer applications. There are some isolated grain disperse on the surface, but this fact does not harm layer functionality. The gold cover is dense and well adhered to the ceramic substrate (Fig. 2b). The estimated, from the cross-section micrograph, layer thickness is ~200 nm (Fig. 2b). Homogeneous grain distribution of particles with 50 nm average dimensions (Fig. 2c) suggests excellent coating properties.

Figure 3 displays the X-ray diffraction pattern of Au layer before CIGS deposition. The sample reveals various diffraction peaks related to SiO₂ (quartz, JCPDS card,
file No 01-083-2471) at 27.1° (2θ) and SiO₂ (cristobalite, JCPDS card, file No 01-076-0939) at 21.8° and 35.8° (2θ). The reflections indexed with (1, 1, 1), (2, 0, 0), (2, 2, 0), and (3, 1, 1) belong to Au (JCPDS card, file No 01-1172). The SiO₂ compounds in the pattern are coming from the glaze layer below. This demonstrates that the Au layer is very thin that may affect to the device properties.

The Au particle sizes were quantitatively evaluated from the XRD data (Fig. 3) using the Debye–Scherrer Eq. (1). From the (1, 1, 1), (2, 0, 0), and (2, 2, 0) d-spacing’s crystallite dimensions were calculated. The particles measure from 20 nm to 50 nm. The result fits well with the microscope observations (Fig. 2c).

X-ray diffractograms of samples A, B, C, D, and E after CIGS thermal treatment are shown in Figure 4. The main diffraction peaks could be assigned to CuIn₀.₇Ga₀.₃Se₂ crystalline phase (JCPDS card, file No 35-1102). It can be notice that reflection intensities increase with temperature changes from 200° to 550°C. Additional peaks at 2θ = 38.3, 64.9, 44.6, and 77° are also found. These reflections could be associated with Au (JCPDS card, file No 01-1172). Diffraction peaks at 2θ = 21.8, 30.8, and 35.7° correspond to SiO₂ (JCDPS card, file No 76-0939) and are coming from the glaze. No secondary phases during the CIGS formation are detected.

Figure 5 shows surface SEM images of CIGS films selenized at different temperatures. The film crystallinity rise with temperature according to XRD results (Fig. 4). Surface (Fig. 5a and b) and cross-section views (Fig. 6a and b) of the films obtained at low temperatures show cracks and pinholes. This result suggests unstick to the substrate coating. To improve the layer, higher temperatures were applied. After treatment, the samples (Fig. 5c–e) show granular surface morphology that decreases with sintering procedure. Finally, well-sintered dense coating with some surface crystals at 500°C (Fig. 5d) is detected. The gold layer thickness decrease from 300 nm (for sample heated at 200°C) to 160 nm (for sample at 550°C) due to
The precursor's decomposition during calcination (Fig. 6). The sample calcined at 500°C displays lack of surface defects, good adhesion to the ceramic substrate and dense, and microstructure. As a result, it was selected among other samples as optimum.

The film elemental composition was determined by energy-dispersive X-ray analysis (EDX). Dotted lines in Fig. 6 indicate the semiquantitative analysis (at.%) of CIGS stoichiometry. The elemental concentration is indicated with dots along the depth in three different areas: bottom (1), middle (2), and top (3). The results in Table I prove a slight Au diffusion toward the CIGS absorber for samples (b), (c), (d), and (e). When temperatures up, the Au diffusion increases and layer thickness decreases (Fig. 6a–e). Nevertheless, the Au diffusion does not have an influence on the optical properties of the CIGS absorber and on the electrical resistance of the back contact. The Au layer still had electrical conductivity that was checked by Multimeter. The optical response is discussed hereafter.

The CIGS sample heated at 500°C presents homogeneous chemical composition (Table I sample d). The extra Cu amount is according to the initial stoichiometry. At lower temperatures (samples a, b, and c), selenium losses are detected. Unexpectedly, more heterogeneous composition for sample (e) is observed despite of the applied higher temperature.

Band gap energy was measured only for sample "d" selected as optimum. Figure 7 shows band gap of approximately 1.18 eV that fits with the value corresponding to Cu(In1-xGax)Se2 solid solution. The result indicates that the detected gold diffusion does not concern the optical properties of the final device.

Figure 8 (a) displays AFM images of the Ag-glazed layer. Polycrystalline silver glaze with heterogeneous and roughness surface is observed. The average roughness is about 14 nm, suitable for layer applications. However, different embedded grains on the surface are detected. Well adhered to the ceramic substrate silver layer is assumed from Fig. 8b and c. Layer thickness ≥2 μm is deduced from the cross-section image in Fig. 8c. Heterogeneous grain distribution with sizes from 3 nm to 500 nm is detected. To confirm the particle dimensions, X-ray diffraction of the Ag layer before CIGS deposition was carried out (Fig. 9). The calculation using Eq. (1) of (1, 1, 1), (2, 0, 0), and (2, 2, 0) exposes crystal sizes cor-

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Fig. 7. Plot of $(\alpha h\nu)^2$ as function of energy for Cu(In, Ga)Se2 sample "d".
responding to 176 nm, 88 nm, and 196 nm that are agreed with the range (3–500 nm) discussed before.

X-ray diffraction spectra of CIGS films treated at different condition are exposed in Figure 10. It can be emphasized that CIGS compound crystalizes even at 350°C (Fig. 10b). The main reflections could be assigned to the CuIn0.7 Ga0.3Se2 (JCPDS card, file No 35-1102). Peaks intensities increase with temperature (Fig. 10b–e). Reflections at 2θ = 38.2, 44.4, 64.6, and 77.5° are related to Ag (JCPDS card, file No 01-087-0718). Secondary phase of Ag2Se compound (2θ = 30.99, 32.78, 33.56, 34.82, 37.04, and 42.73°) (JCPDS card, file No 00-020-1063) is also distinguished. This result concludes that Ag diffuse toward the absorber layer (Table II). Diffraction peaks at 2θ = 21.8, 30.8, and 35.7° is assigned to SiO2 (JCPDS card, file No 76-0939).

Scanning electron microscopy surface images of CIGS films treated at different temperatures are exposed in Fig. 11. Granular surface morphology and increasing with temperature grains can be observed. Sintering processes at higher temperatures are deduced (Fig. 11c and d). The cross-section micrographs on Fig. 12 show unstuck to the substrate coatings for all temperatures. This result could be ascribed to the way of deposition (e.g., screen printing). Holes and irregular morphology for all samples are remarked. The layer’s elemental composition (Table II) confirms silver diffusion and heterogeneities. The silver enamel is unstable under thermal treatment. The layer results nonohmic. Any further characterization for the Ag system was avoided.

Conclusions

Gold and silver enamels were developed as potential back contacts for CIGS solar cells. The enamels were successfully deposited on ceramic substrates making integrated photovoltaic tiles for the first time. The substrates evidence lack of porosity, mechanical and chemical resistance, and low linear contraction. Different methods of
Table II. EDX Analysis (at.%) and Metal Ratio of Sample Heated at: (a) 200°C, (b) 350°C, (c) 450°C, (d) 500°C, and (e) 550°C

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Fig. 11. Scanning electron microscopy (SEM) surface images of samples heated at: (a) 200°C, (b) 350°C, (c) 450°C, (d) 500°C, and (e) 550°C.
enamel deposition, ink-jet and screen printing, were applied. The ink-jet proves better effectiveness than screen printing.

Nonvacuum routes for CIGS synthesis (coprecipita-
tion) and deposition (doctor blade) were used. The coprecipitation of selenite precursors results very successful obtaining CuIn$_0.7$Ga$_{0.3}$Se$_2$ solid solution. Doctor blade technique achieved well-adhered, dense, and homogeneous layers with adequate thickness.

Excellent compatibility between CIGS and gold coating was obtained keeping layer width and chemical composition adequate for photovoltaic applications. The band gap measurement confirms the assembly effectiveness.

In contrast, silver diffusion leading coating separation was achieved for the silver glaze. The Ag layer results nonohmic and therefore the back contact unusable.

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