# PHOTOVOLTAIC CERAMIC TILE BASED ON THIN FILMTECHNOLOGY

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## 1. ABSTRACT

This paper sets out an overview of the different projects being conducted by the Solid State Chemistry Group at Universitat Jaume I for the development of thin film photovoltaic cells on ceramic substrates. The use of ceramic tiles as an alternative to the soda–lime glass substrate customarily used in photovoltaic devices seeks to contribute high added value to traditional flat ceramics, enabling integration into architectural environments for the generation of electric power from sunlight. The photovoltaic tiles are obtained through the heterjunction of conducting and semiconducting thin film materials, based mainly on the chalcogenide materials CIGS and CZTS, to generate the photovoltaic effect. The most significant results obtained in the different projects are also reported.

## 2. INTRODUCTION

The photovoltaic industry's main objective, nowadays, is to reduce production costs in order to bring a product to market that can compete directly with the other energy sources. The investigations in this field have led to the second generation of photovoltaic cells [1]. These cells are particularly intended to decrease production costs, their general principle being replacement of the expensive materials used by crystalline silicon technologies with other, cheaper ones. Several technologies have thus emerged, among which the chalcogenide-based technology is particularly noteworthy [2]. Chalcogenide cells work with an extremely thin layer of semiconducting material, which is mainly applied on a soda–lime glass substrate. This technology provides greater automation when a sufficiently large level of production is reached, concurrently allowing a more integrated approach in the construction of modules. As a result, labour costs are significantly lower than those in the crystalline module manufacturing process.

At present, photovoltaic solar devices are used in a great number of applications, an important use being their integration in buildings, i.e. as building integrated photovoltaics (BIPV)[3]. The incorporation of these devices entails the replacement of conventional construction materials with new photovoltaic architectural elements, providing an important source of electric power and energy saving.

This paper sets out an overview of three projects that are being carried out by the Solid State Chemistry Group at Universitat Jaume I, in collaboration with various leading companies and research groups, to obtain thin film photovoltaic devices based on the absorbent materials CIGS ($Cu(In,Ga)Se_2$ [4] and CZTS ($Cu_2ZnSn(S,Se)_4$on alternative substrates [5]. The three projects have in common the study of the use of porcelain tiles as substrates for solar cell assemblies, in order to reduce production costs and provide ceramics with greater added value, enabling them to be integrated into the urban architectural environments (BIPV) for the generation of photovoltaic solar energy. On an environmental level, these projects are also intended as examples of the reuse of industrial wastes as raw materials in the manufacturing process of substrates for thin film photovoltaic cells. The industrial wastes that could be valorised in the formulation of the bodies corresponding to these substrates are as follows: recycled glass, fritted material from glaze production wastes, ceramic tile waste, slag from thermal power stations and/or blast furnaces, etc. Consequently, the development of photovoltaic cells, on green ceramic and glass-ceramic substrates (obtained by incorporating raw materials from industrial wastes), will involve the development of innovative ceramic products with high added value for the national ceramic industry, providing new opportunities for this sector.

## 3. PHOTOVOLTAIC DEVICE COMPONENTS

The components of a photovoltaic cell based on thin film technology are shown in Figure 1.

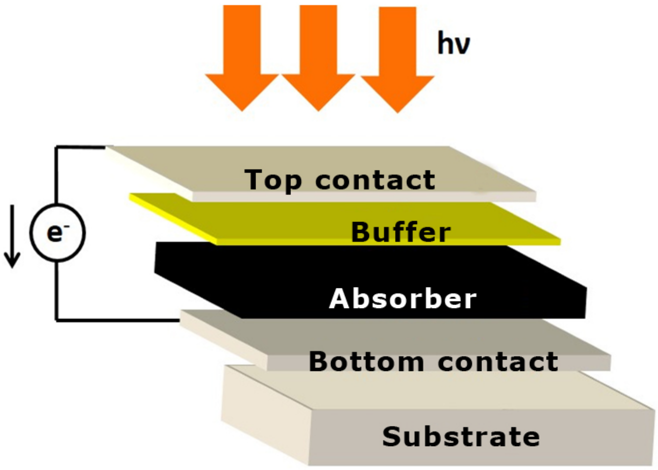


***Figure 1.*** *Cross-sectional scheme of a thin film-based photovoltaic device.*

- **Substrate**: Owing to the nature of the thin films used in the development of photovoltaic cells, the films can be deposited on different types of substrates, ranging from traditional soda-lime glass [6] to polymer [7], metallic [8]or ceramic substrates [9]. The substrate must provide an appropriate surface for the deposition of all the active layers, meeting requirements such as low or zero roughness, inertness with regard to the material to be deposited, thermal stability, zero porosity, and an appropriate coefficient of thermal expansion compatible with the other cell components [6].

- **Bottom contact:** The bottom contact consists of a thin film(800 nm thick) of metallic molybdenum deposited by magnetron sputtering (cathode spraying). This shall exhibit low or zero reactivity with the absorbent film, good electrical conductivity, and an appropriate coefficient of thermal expansion with the other components [10].

- **Absorbent film**: Ap-type semiconducting material is deposited on the molybdenum film, in the form of a thin film about 2 μm thick, as CIGS ($Cu(In,Ga)Se_2$ or CZTS ($Cu_2ZnSn(S,Se)_4$). These materials exhibit many similarities in both crystal structure and electrical behaviour and the same multilayer arrangement is currently being used in manufacturing the photovoltaic device [6]. Therefore, depending on the photo-absorbent material used, the photovoltaic devices will be CIGS or CZTS. These materials are capable of absorbing electromagnetic radiation and promoting electron movement. The method of obtaining both compounds can be separated in high vacuum [11] and by chemical routes [12], both similarly needing a thermal treatment at about 500ºC, in the presence of chalcogenides (Se, S, or both) to crystallise the corresponding phase. At present, maximum efficiencies of 21.1% for solar cells based on CIGS and of 12.6% for CZTS on a soda-lime glass substrate have been reported [13].

- **Buffer film:** The buffer film consists of an n-type semiconductor, capable of creating the p–n bond with the photo-absorbent film. In this case, a 50-nm thin film of CdS is used, most commonly deposited by chemical bath owing to the simplicity of the method and its good results, though it is not the only method used [14]. In CdS deposition by chemical bath, it is important to take into account factors such as substrate roughness, which conditions the choice of cadmium salt used. The use of CdS as buffer film provides higher photovoltaic efficiencies in CIGS and inCZTS.

- **Window film**: The window film consists of a 50-nm film of intrinsic ZnO and a 60-nm film of ITO ($In_2O_3$ 10%-$SnO_2$ 90%). Both films are deposited by magnetron sputtering [5]. These films are capable of conducting electricity and also allow the passage of electromagnetic radiation in the visible zone, owing to their high band gap. The use of high vacuum methods, which largely reduce the thermal treatment temperature, is necessary in the last process stage, because the crystallisation of ZnO and of ITO, without high vacuum, would give rise to inter-film diffusion processes that might damage the device.

## 4. ONGOING PROJECTS FOR THE DEVELOPMENT OF PHOTOVOLTAIC TILES

This section briefly describes each of the projects aimed at obtaining photovoltaic tiles being conducted by the Solid State Chemistry Group at Universitat Jaume I.

### 4.1. ECOART PROJECT

The project with acronym ECOART is funded by the Spanish Ministry of Economy and Competiveness (MINECO) under the programme **RETO COLABORACIÓN**, and consists of a consortium of research centres, including universities, and private companies. In this project, the collaborating organisations are UJI (Universitat Jaume I) and IREC (Institut de Recerca en Energia de Catalunya) as research centres, while the participating companies are the Torrecid Group, Camacho Recycling S.A., FAE and Invest Plasma. The project seeks to develop photovoltaic tiles measuring 10 x 10 cm. To do so, glass-ceramic and ceramic substrates are being developed from wastes from the ceramic sector itself and also from the recycled glass sector, compatible with architectural functionalities. It is thus intended to optimise the use of natural resources and concurrently avoid the pollution stemming from these wastes. With regard to their full compatibility in a ceramic production process, the development of alternative bottom contact layers to conventional molybdenum films is being studied, based on the integration of conducting glazes. This objective is particularly innovative and will suppress the need to use the expensive and complex vacuum methods that are currently required for Mo film deposition, consequently contributing to a significant reduction in costs.

For the study of the absorbent film, the CIGS and CZTS chalcogenide systems are being used, and the synthesis and deposition of both compounds is being studied, through more efficient and environmentally sustainable methods, based on the use of chemical strategies that do not require high vacuum stages and are characterized by a very high efficiency in the use of the materials (typically above 90%). In this case, there is a special emphasis on the development of scalable technologies compatible with their industrial implementation, based on inkjet printing processes. On the other hand, the study also addresses the replacement of the CdS buffer film that uses an element of high toxicity (CD) with other, more harmless films such as ZnS, ZnSe, and $In_2Se_3$. In the final project phase it is intended to develop demonstrators of the proposed technologies, making photovoltaic modules with an intermediate surface area (20x30 cm), integrating mini-modules of 10x10 cm and studying their architectural integration in buildings for BIPV applications.

### 4.2. SUNBEAM PROJECT

The project with the acronym SUNBEAM is funded by the MINECO under the programme **RETO INVESTIGACIÓN**, in which only research centres, including universities, are allowed to participate. The project partners are UJI (Universitat Jaume I), IREC (Institut de Recerca en Energia de Catalunya), UAM (Universidad Autónoma de Madrid), and UB (Universitat de Barcelona). It is sought to develop photovoltaic solar cells based on CZTS photo-absorbent material by various methods. As already noted in the previous section, the methods of obtainment of CZTS material are mainly divided into methods using high vacuum and chemical routes. In the Solid State Chemistry Group an alternative method is pursued, based on chemical routes, involving the synthesis and deposition of selenites of the corresponding metals. However, at the IREC and the UAM, high vacuum physical methods such as sputtering and co-evaporation are being developed, due to their extensive knowledge in this field. The use of different methods allows them to be compared and the best to be chosen for future scalability of the device, taking into account factors such as price, pollution, stability and efficiency of the photovoltaic device. On the other hand, the project pursues the use of alternative substrates to soda-lime glass, such as porcelain tile, and flexible substrates, such as polyimide and thin sheet steel, which could be used in aerospace applications owing to their low weight.

### 4.3. SUNCERAM PROJECT

The project with the acronym SUNCERAM is funded by Universitat Jaume I under the **STARTUJI** projects. In this third project, the Solid State Chemistry Group is the sole participant, though it enjoys the help and support of the companies and research groups involved in the projects mentioned above. The SUNCERAM project pursues obtainment of photovoltaic tiles based on CIGS photo-absorbent material and the study of their stability and integration into architectural environments, with a view ultimately to finding a commercial application of these prototypes in the near future. In this project, it is sought to highlight not just the fabrication of the photovoltaic device, but the entire subsequent process of interconnection, encapsulation, and integration to obtain optimum photovoltaic modules for installation.

## 5. MOST NOTEWORTHY RESULTS

This section sets out the most noteworthy results with regard to the fabrication of photovoltaic ceramic tiles. As preliminary results of the above projects in which the Solid State Chemistry Group is working, thin film photovoltaic devices have been satisfactorily completed using CIGS and CZTS materials as photo-absorbers, obtained through the synthesis and deposition of metallic oxides.

Figure 2 shows the SEM characterisation of the different stages in the CZTS film obtainment process from metallic oxide deposition. To do so, a precursor powder was obtained first by coprecipitation, in which the metal oxides of copper, zinc and tin precipitated jointly (Figure 2a). The precursor powder, after dispersion in an organic medium such as ethanol, was deposited as a thin film (Figure 2b) on the porcelain tile substrate coated previously with molybdenum. After deposition of the precursor material, a thermal treatment was required to obtain the kesterite crystal phase, responsible for the photovoltaic effect (Figure 2c). The crystallisation of the photo-absorbent film occurred mainly at the surface, as may be observed in Figure2d, which is characteristic of the methods based on chemical routes and is the main cause of photovoltaic conversion.

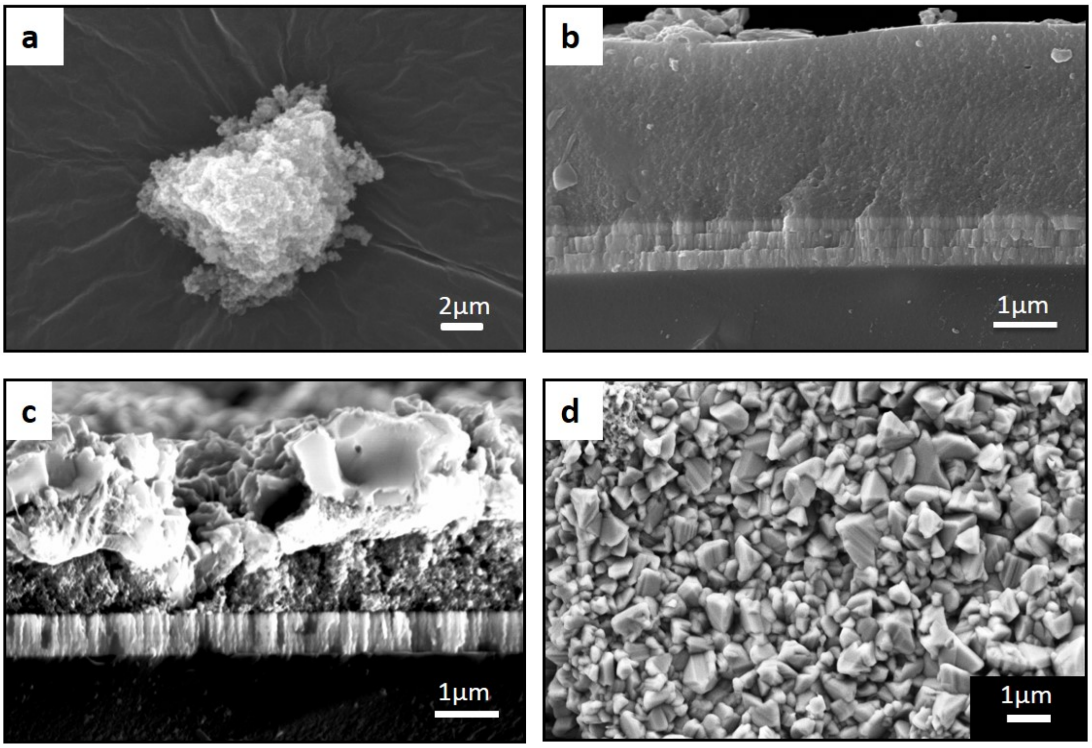


***Figure 3.****SEM micrographs of* ***a)*** *CZTS precursor powder,* ***b)*** *cross-section of the CZTS precursor film after deposition,* ***c)*** *cross-section of the film after thermal treatment, and* ***d)*** *surface of the crystallised CZTS film.*

Figure 3a shows an example of a photovoltaic ceramic tile measuring 2.5 x 2.5 cm based on CZTS photo-absorbent material after deposition of the CdS buffer film, the ZnO/ITO window film, and mechanical scratching. Figure 3b depicts a micrograph of the cross-section of the same photovoltaic ceramic tile. The micrograph shows the array of films that make up the cell, in which the soda-lime glaze may be noted. The glaze enhances the surface properties, contributing low roughness, impermeability, and chemical inertia with relation to possible chemical attack. The molybdenum bottom contact with a thickness of about 800 nm can be observed on the glaze. The 2-µm-thick film CZTS can then be seen, and finally the buffer and window films which, owing to their thinness, cannot be well distinguished in this micrograph.

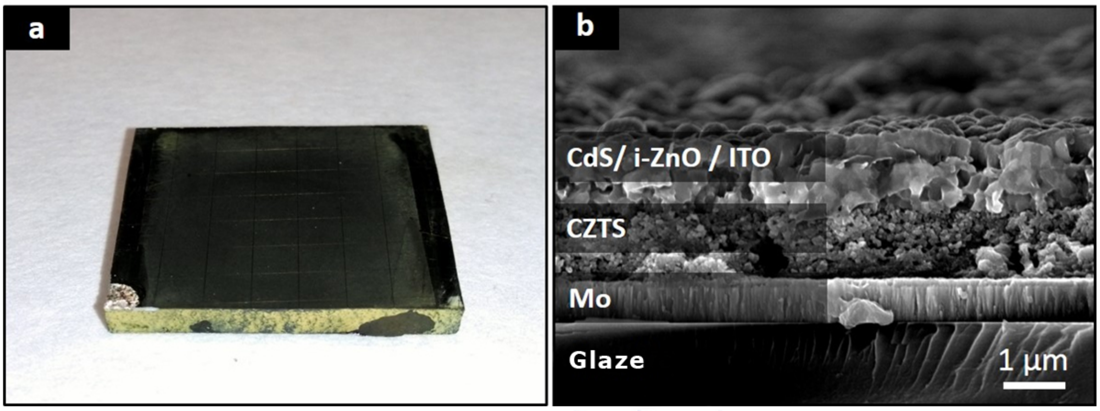


***Figure 3. a)*** *Digital image of the photovoltaic tile;* ***b)*** *SEM cross-section of the photovoltaic tile.*

A photovoltaic conversion efficiency of 1.3% was found for CIGS and of 2% for CZTS. Despite this low output, the result is hopeful, owing to the preliminary state of the work. It may be noted that in this type of CIGS and CZTS photovoltaic cells, every factor, from the substrate to the window film, can significantly influence the eventual efficiency of the photovoltaic device so that it is very important to control all the parameters.

## 6. CONCLUSIONS

The obtainment of photovoltaic tiles is intended to contribute added value to the traditional ceramic product from Castellón province. The use of thin film technology allows integration of the films responsible for the photovoltaic effect on the ceramic glaze itself. The films responsible for absorption are based on CIGS and CZTS chalcogenide compounds. These devices can be integrated into the architectural environment for BIPV applications, thus reducing costs in building construction, owing to the replacement of traditional construction materials with devices capable of generating electricity. The results obtained to date are hopeful with regard to the continuity of the projects and to possible commercial use.

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