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Microwave calcination of thin TiO_2 films on transparent conducting oxide glass substrates

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Transparent conducting oxide (TCO) coated glass is used for many different purposes such as substrates for solar cells [1–3] and electrochromic windows [4]. The use of such substrates is imperative for the flow of electrons to allow the functionality of these devices. For these devices to operate efficiently, calcination in a conventional oven is usually employed after deposition of the functional materials onto the TCO glass. However, microwave heating offers many advantages as an alternative. In the case of microwave heating, materials can reflect, absorb or be transparent to microwaves [5]. Thus, only materials that absorb microwaves are heated. Microwave processing has the characteristic of rapid heating rates and efficient heating, promoting sintering at lower temperatures and in shorter times compared with conventional processes [6]. However, some key processing issues remain with regard to TCO coated substrates which are necessary and we describe a method for overcoming these problems.

In this study, fluorine-doped tin oxide ($F{:}SnO_2$) coated glass (Hartford Glass) was used as the TCO substrate. A 2.45 GHz microwave furnace (MPC, Model 941) was used with variable power up to 1 kW and a three-stub tuner. A power of 500 W was used until the sintering temperature of 450 °C was reached. The power was then adjusted to ensure that $450 \pm 5\,^{\circ}C$ was held constant for 15 and 30 min. TiO_2 coatings were deposited with an aqueous slurry of TiO_2 powder (P25, Degussa) using a doctor blade technique. These films were cut to $0.25\ cm^2$ and sintered either using the microwave technique for 30 min or in a conventional furnace at 450 °C for 30 min, as a comparison. Some electrodes had a further heat treatment via either technique at 450 °C for 15 min. Dye adsorption was achieved using a 3×10^{-4} M acetonitrile (Merck, 99.98%) solution of N3 ($[Ru(dcbpy)_2(SCN_2)]$ where dcbpy = 4,4′-dicarboxylic acid-2,2′-bipyridine) for 18 hrs at room temperature. The working electrodes were attached to the thermally platinized counter electrode with Surlyn film (Dupont) and electrolyte [0.5 M LiI (Lancaster), 0.04 M I_2 (Lancaster) and 0.05 M 4-*tert*-butylpyridine (Aldrich) in acetonitrile] was infused via capillary forces.

When the specimen was initially heated in the microwave, it was found that at temperatures exceeding 200 °C, the TCO film was cracking (Fig. 1A and B). This lead to further studies to investigate the nature of the failure which is catastrophic in terms of further use of such a substrate in an electronic device. Fig. 1A shows the TCO glass alone exposed to microwaves and photographed from an aperture where the light source was in the furnace itself (bottom left direction from the TCO glass). Fig. 1B is the same TCO glass after removal from the furnace taken under an optical microscope. All photos were taken on a cordierite refractory brick.

The cracking of the TCO coating caused arcing across the crack due to the conductive nature of the film. In extreme circumstances it was noticed that the glass began to melt at the crack interface. This is further indirect evidence that a local field is present that leads to arcing across the cracks. It resulted in a detrimental reduction in the conductivity of the TCO film, in the worst case becoming insulating.

Since microwaves only heat the TCO coating [7], the underlying glass substrate will only be indirectly heated through thermal convection from the TCO. With a significant heating rate, this leads to a thermal gradient in the glass where the maximum is at the TCO coating, resulting in interfacial cracking. Interestingly, in conventional heat treatments no problems arose as the glass and TCO film were heated simultaneously. Thus, the microwaves are clearly selective in their heating of the TCO coating.

To overcome this problem a jig (Fig. 2) was made from clay and fired at 1200 °C. The concept was to provide a homogenous heating zone into which the TCO glass is inserted. This heating zone was generated by the use of two beds on either side of the glass of silicon carbide (SiC), which are readily heated in the presence of 2.45 GHz microwaves [8, 9]. This jig (Fig. 2) allows for radiative heating of both the TCO film and the glass simultaneously. Thus, if the heat provided by the SiC is homogenous and heats at a faster rate than the TCO film itself, then cracking of the TCO film can be avoided. The importance of the proposed processing geometry is that whilst the microwave continues to interact with the functional material, it also provides the energy to heat the SiC to provide the heating of the TCO and glass substrate to minimise cracking. In addition, it may be found that the temperature or time may be decreased providing similar sintering to that seen in a conventional furnace.

Heating of a new set of films at 450 °C for 15 min in the microwave was carried out using the jig. It was found that the cracking was avoided with no increase in the resistance of the substrate surface or evidence of cracking of the film (Fig. 1C).

When applied to sintering of 10 μm thick TiO_2 electrodes, which were used to construct dyesensitized solar

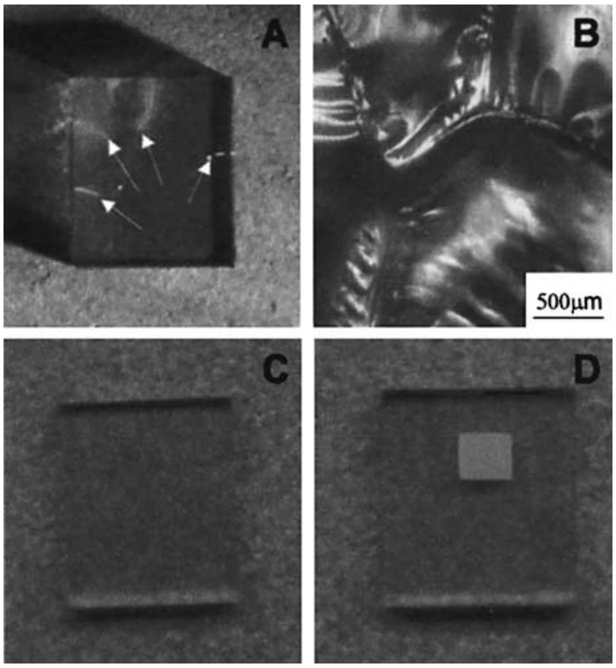

Figure 1 (A) TCO-coated glass piece in a 2.45 GHz microwave furnace at approximately 300 °C cracking and arcing (arrowed) and (B) an optical microscope image after heating, displaying cracks throughout the film. (C) Uncracked TCO glass and (D) Uncracked TiO_2-coated TCO glass where (C) and (D) were heated in the newly designed jig at 450 °C for 30 min in the microwave oven.

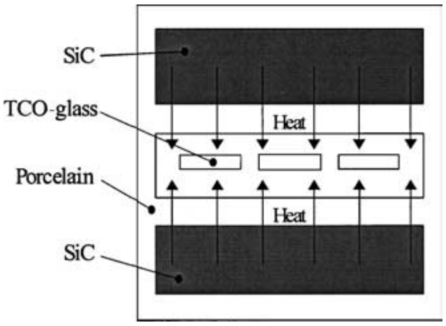

Figure 2 The jig produced to microwave TCO-coated glass and DSSC electrodes.

TABLE I Photovoltaic characteristics of TiO_2 electrodes sintered under various conditions

Electrode	V_{oc}(mV)[a]	J_{sc}(mAcm^{-2})[b]	FF[c]	η(%)[d]
Conventionally heated at 450 °C for 30 min	720	6.79	60	3.02
Microwave heated at 450 °C for 30 min	745	6.08	64	2.89
Conventionally heated at 450 °C for 30 min followed by conventional heating at 450 °C for 15 min	725	6.72	61	2.99
Conventionally heated at 450 °C for 30 min followed by microwave heating at 450 °C for 15 min	745	6.37	62	2.95

[a] V_{oc} is the open circuit voltage.
[b] J_{sc} is the short circuit current density.
[c] FF is the fill factor.
[d] η is the overall conversion efficiency.

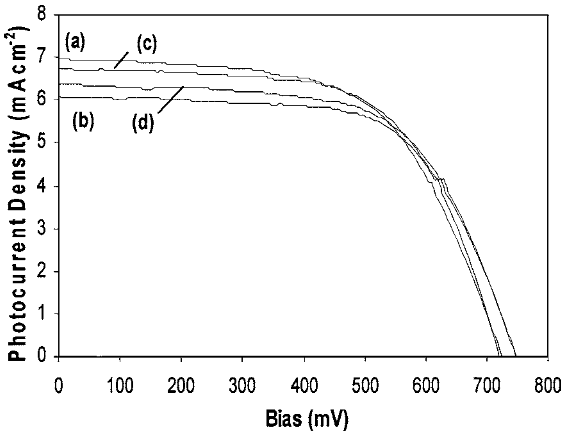

Figure 3 IV Curves for the electrodes produced from electrodes: (a) conventionally sintered for 30 min, (b) microwave sintered for 30 min, both at 450 °C. (c) and (d) are conventionally sintered then further conventionally sintered for 15 min and microwave sintered for 15 min, respectively.

cells (DSSCs), the same result was obtained (Fig. 1D). The IV curves (Fig. 3) for the electrodes sintered in the microwave and conventional furnaces display similar characteristics. It should be noted that all cells have a high open circuit voltage but it can be seen that the greatest current was observed with the electrodes that were sintered conventionally for 30 min at 450 °C.

Table I shows that after microwave sintering the open circuit voltage is increased to 745 mV. In addition, the current from the electrodes sintered for 30 min by microwaving was lower than the conventionally sintered electrodes. This, perhaps, indicates that the process may require an optimized time and temperature to achieve the same level of sintering, as over-heating could result in a low electrode surface area and low current. Thus, a higher temperature may be required for the TiO_2 film to provide necking of the nanoparticles to form a good semiconductor nanostructure. The electrodes produced in this study all yielded cell efficiencies that were within experimental error. The net result of changes in the IV profile, open circuit voltage and the short circuit current being that the overall efficiency of the cells does not change significantly (2.9–3%).

This simple technique allows us to further examine the use of microwave sintering of thin films on TCO glass. The ability to use microwaves as a processing tool could lead to a decrease in the sintering time and/or temperature required to effectively heat-treat certain materials. This would, in turn, decrease the cost of manufacturing thin films on conductive glass substrates. In addition, microwaves could be used to sinter coated semiconductor films to form core-shell nanostructures. If the shell material is a microwave absorber then it could be possible that densification of the shell could be selectively enhanced by microwaves, which is currently unachievable by conventional processing [10].

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