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Recycling of Photovoltaic Modules – a Strategy for Silicon and Metal Contact Recovery

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Abstract. As the installed capacity of photovoltaic (PV) systems continues to grow, also does the necessity to address the accumulating waste from decommissioned PV modules. Millions of modules will need to be retired in the next few decades, and this poses a challenge that requires the development of cost-effective and efficient recycling strategies, with a focus on essential components such as solar cells, which are known for their significant environmental impact and energy budget. This study explores strategies to recover metal from front and rear contacts, as well as the potentiality of silicon substrate recrystallization. Alkaline-organic solutions allow for complete metal detachment with small-to-minimal silicon loss, and recrystallization of recovered substrates provides promising results in obtaining wafers suitable for the newly established industry requirements. Al-BSF solar cells fabricated from recycled materials exhibit improved performance, proving the feasibility of reclaiming precious metals and silicon substrates from PV modules. These encouraging first results represent an important step towards cycling PV systems within a circular economy framework, thereby minimizing waste and maximizing resource utilization.

Keywords: Silicon, Solar Cells, Recycling, Recrystallization, Metal Recovery

1. Introduction

The evergrowing photovoltaic (PV) industry is expected to reach tens of terawatts of installed capacity by 2050 [1], [2]. Due to the limited lifetime expectancy of modules, millions of tons of decommissioned PV components – which are mainly composed of silicon-derived technologies – will be expected to be processed accordingly, raising the need for efficient, cost-effective and environmentally conscious recycling strategies.

While current strategies already exist for the recycling of PV technology, most of them are based on weight, that is, they focus on the more massive components of the modules, mainly aluminum frames and glass covers. More attention needs to be put on the recycling of the most costly components of the modules: the solar cells. The establishment of practical routes for the reutilization silicon substrates would also lead to highly reduced energy consumption and CO_2

emissions in the PV value chain due to avoiding ultrapurification process. It is also crucial to implement strategies that would allow for the reutilization of valuable materials such as aluminum and silver, which present significant usage in the PV industry; for instance, 12.7% of the annual silver production of the year 2020 was devoted to solar cell manufacturing [3]. The preservation of these valuable and scarce materials is crucial in order to maintain availability given the growing trends of the industry.

In this work efforts were put into developing a recycling strategy that will allow for two main objectives: (i) recover metallic species from the contacts and allow their reuse; and (ii) minimize the substrate losses in order to be able to reintroduce recovered substrates into the PV value chain.

2. First phase of experiments: demetallization

Preliminary studies on metal recovery from solar cells involved acid leaching process from fragmented devices from TiO_2 ARC solar cells [4], [5]. While considerable rates of success were achieved (up to 94%, [6]), the substrate recovery rate is null, not allowing for recrystallization.

In this work, the use of KOH-ethanol-water solutions, similar to those used in wafer texturization, are explored in order to physically remove metal contacts. KOH-ethanol-water solutions work through the interaction of silicon and aluminum surfaces with water and KOH, while the ethanol acts as a control of the etching rate. The processing conditions (temperature, time and concentration) are optimized with a threefold purpose: (i) achieve full removal of front and back contacts; (ii) complete dissolution of the antireflective (ARC) layer; and (iii) minimal Si substrate loss.

The optimization was performed following the design-of-experiment methodology, following a 2^3 experimental design with central point replication. After optimization, it was concluded that two alternative processing conditions allow the objectives previously established: (i) 10% KOH, 5% ethanol and 60ºC for 105 minutes; or (ii) 15% KOH, 5% ethanol and 65 ºC for 60 minutes. Both options allow for complete detachment of the metal front and rear contacts with reduced Si loss, 13% and 15% respectively. QSSPC lifetime measurements [7] were performed with the Sinton WCT-120 setup on silicon fragments after metal detachment as a means to assess the surface contamination and material quality. With iodine-ethanol (IE) passivation, values consistently above 100 µs were obtained, that would allow for efficiencies above 20% [8].

Experiments were carried out in cut fragments from old solar cells manufactured by the company Isofotón back in the 1980s, with front contacts made from a silver screen-printing paste, and rear contacts presenting traces of aluminum, iron and lead as well. The thickness of the treated fragments before processing was 350 µm including the metallic contacts, and a weight of approximately 1 g. Figure 1 represents the demetallization process, showing the setup (1a), the fragments before and after processing (1b and 1c), and the detached contacts (1d).

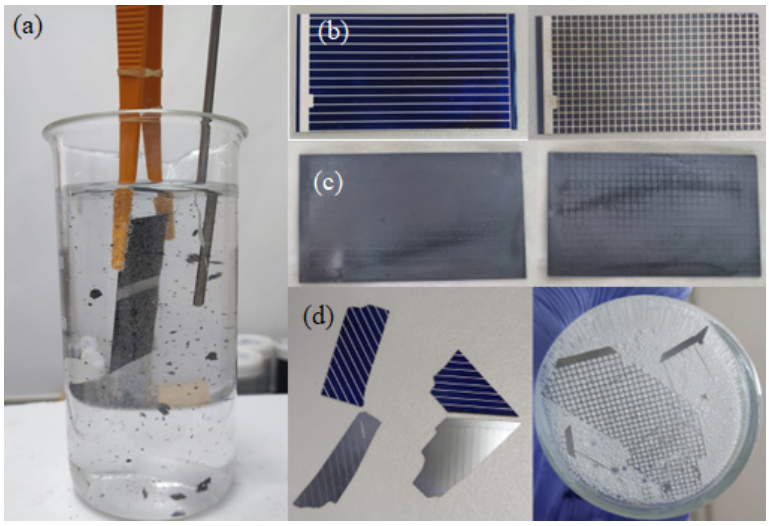

Figure 1. *(a) Demetallization setup. (b) Samples before demetallization, front and back side. (c) Samples after demetallization, front and back side. (d) Detached metallic contacts.*

Cell fragments were analyzed through SEM/EDX measurements in order to determine the localization of metals. Figure 2 shows SEM and EDX images of the front and rear sides of a cell fragment. The cell surface has the typical pyramidal morphology resulting from an alkaline texture.

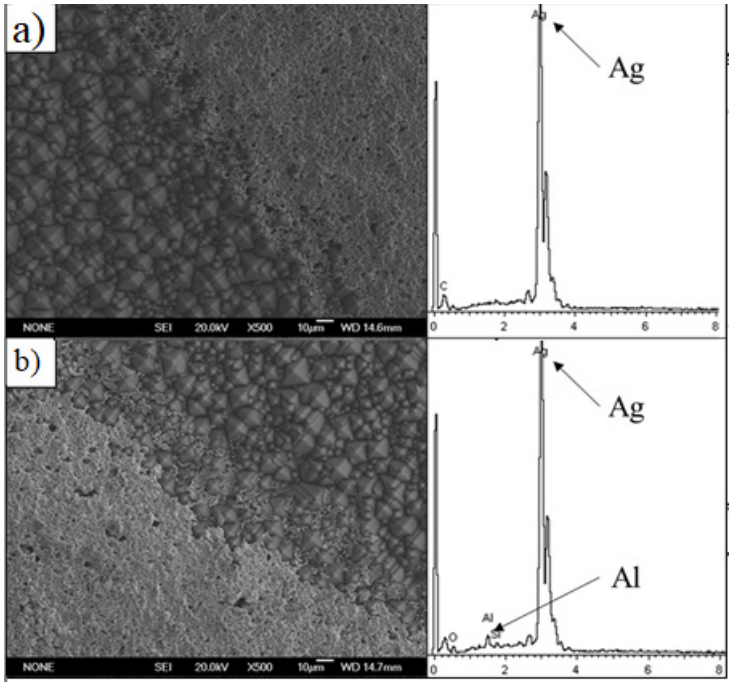

Figure 2. *EDX/SEM images of the (a) front and (b) rear contacts of a solar cell before demetallization.*

Before demetallization, the analysis concluded that silver is present in both front and rear contacts; whereas aluminum is only located in the rear contact area. No other metals were found in the metallic contacts.

The detached metallic contacts were analyzed through X-Ray Fluorescence (XRF) in order to identify the metals present and Atomic Absorption Spectrometry (AAS) in order to determine the silver concentration after complete acid digestion with 3M nitric acid. XRF measurements are presented in Figure 3.

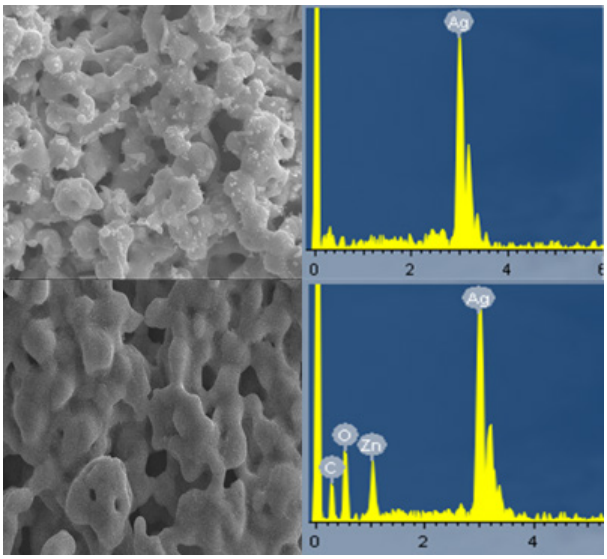

Figure 3. *XRF measurement of detached front and rear contacts.*

The analysis yielded very high concentrations of silver (up to 100% in the front contacts and 98% in the back contact). No traces of frits can be found in the detached contacts and small traces of carbon and oxide can be located in the back contacts. As no traces of elemental aluminum can be found in the XRF measurements, it is assumed that the traces of aluminum deposited in the back contact are diluted in the digestion solution. No traces of Si are observed, which leads to the conclusion that the contacts were fully detached.

3. Second phase of experiments: recrystallization

The second part of this work focuses on the recrystallization of old p-type multicrystalline wafers into monocrystalline p-type wafers.

While multicrystalline substrates were the backbone of the PV industry for decades, today's market is dominated by monocrystalline substrates. For this reason, a (100) Cz-mono ingot (Figure 4b) was grown using 150 grams of multicrystalline wafers from the 2000s (Figure 4a), which was then wafered into 80 500 µm samples (Figures 4c and 4d) and characterized through resistivity and lifetime measurements.

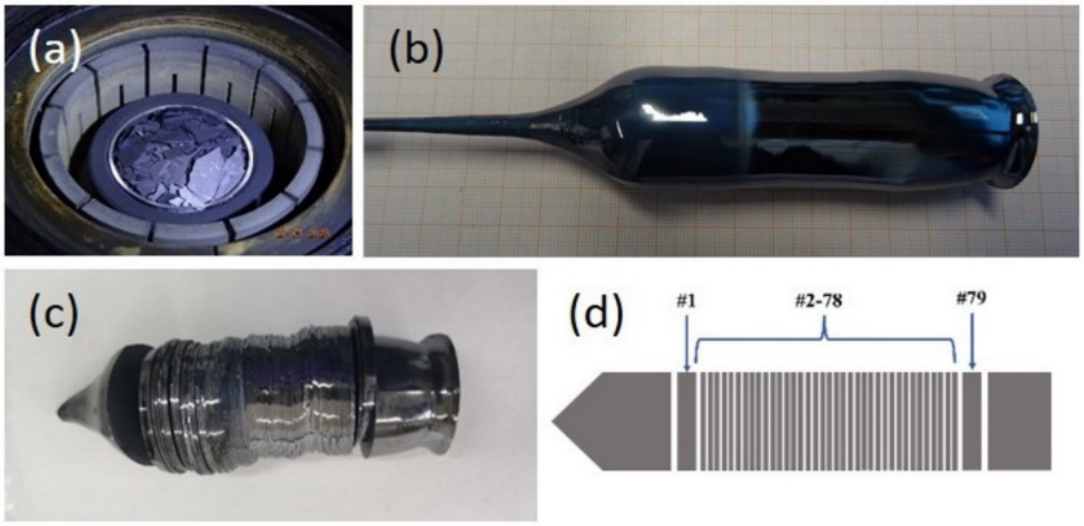

Figure 2. *Steps of the recrystallization process: (a) multicrystalline fragments introduced in the crucible, (b) grown Cz-ingot, (c) wafered ingot and (d) schematic numbering of the wafers.*

After wafering, samples were treated with acetone and IPA rinsing and degreasing detergent; as well as CP4 and RCA1 treatments. Resistivity was obtained by four-point probe measurements along the height of the ingot in order to observe the effect of dopant segregation. Resistivity values ranged from 0.95 to 0.72 Ω·cm along the ingot, and results that were fitted to the Scheil's model [9] for segregation.

From this fit, a boron concentration between 1.6×10^{16} cm^{-3} and 2.1×10^{16} cm^{-3} (top and bottom of the ingot, respectively) is obtained. This value correlates well with the original resistivity of the multicrystalline samples used to grow the ingot.

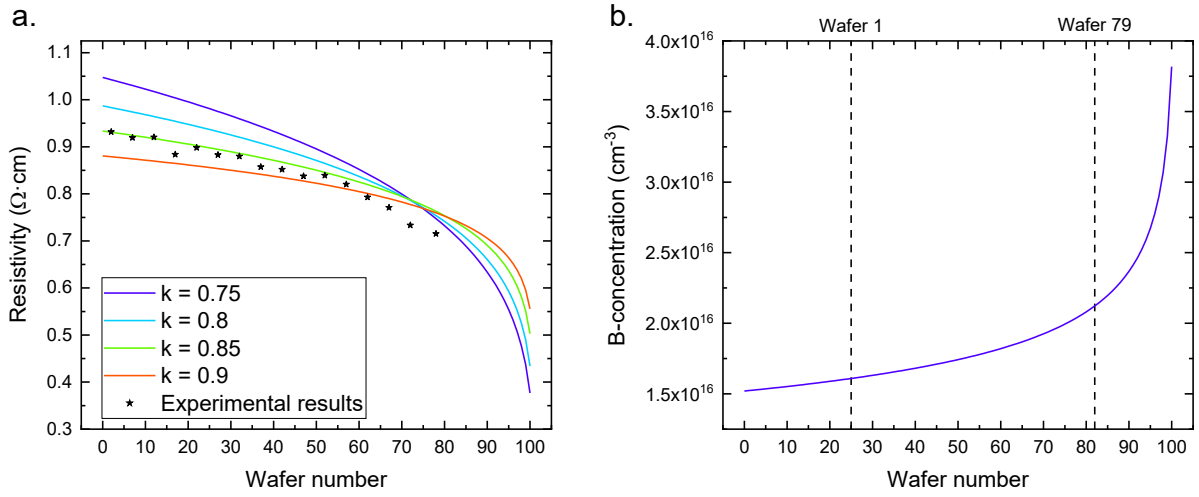

Figure 3. *(a) Resistivity measurements (black stars) and fits to the Scheil's model of dopant segregation. (b) Variation of the concentration of B along the Cz-ingot.*

Carrier lifetime measurements were performed, as shown in Figure 6, after IE passivation. Figure 6a corresponds to injection-dependent carrier lifetime measurements, while Figure 6b shows values measured at a fixed injection point of 1×10^{15} cm^{-3} for the original multicrystalline wafers (black) as well as the recrystallized wafers before (blue) and after (green) a P-diffusion gettering (PDG).

The PDG, an effective technique at removing possible impurities introduced in the wafer bulk during crystallization, was performed due to the reduced carrier lifetimes shown by the recrystallized wafers, ranging from 5 to 40 µs compared to values ranging from 60 to 114 µs for the original multicrystalline wafers. The P-diffusion gettering was performed in a tubular quartz furnace, at 865ºC during 60 minutes, followed by a 10-minute drive-in. After the PDG, recrystallized wafers reached lifetime values among 150 and 350 µs, values that would allow for the fabrication of high-efficiency devices [8] and that entail a significant improvement from the original multicrystalline samples.

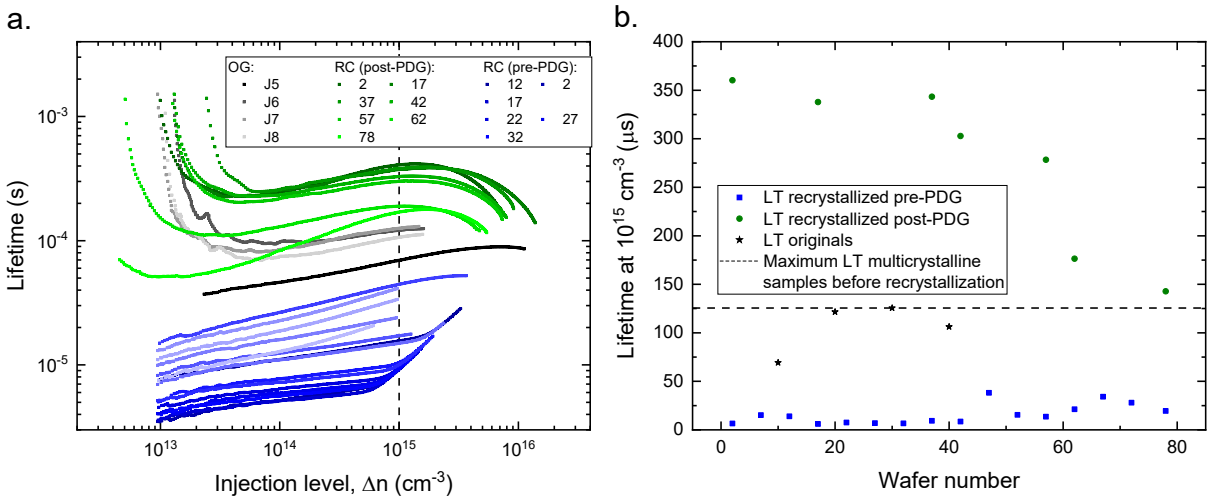

***Figure 4**. (a) Effective carrier lifetime as a function of the injection level for the original multicrystalline samples (black), recrystallized samples before a PDG (blue) and recrystallized samples after a PDG (green). (b) Effective carrier lifetime values at a fixed injection level of 1×10^{15} cm^{-3}.*

4. Characterization of devices

Conventional P-diffused emitter, Al-BSF solar cells were manufactured on six of the monocrystalline recrystallized wafers, as well as on one of the multicrystalline wafers used for recrystallization and one 5x2.5 cm^2 monocrystalline demetallized fragment from the previous section for comparison purposes. Further detail on the manufacturing of the solar cells can be found elsewhere [10]. I-V curve and external quantum efficiency (EQE) measurements of said cells were performed and are shown in Figure 7.

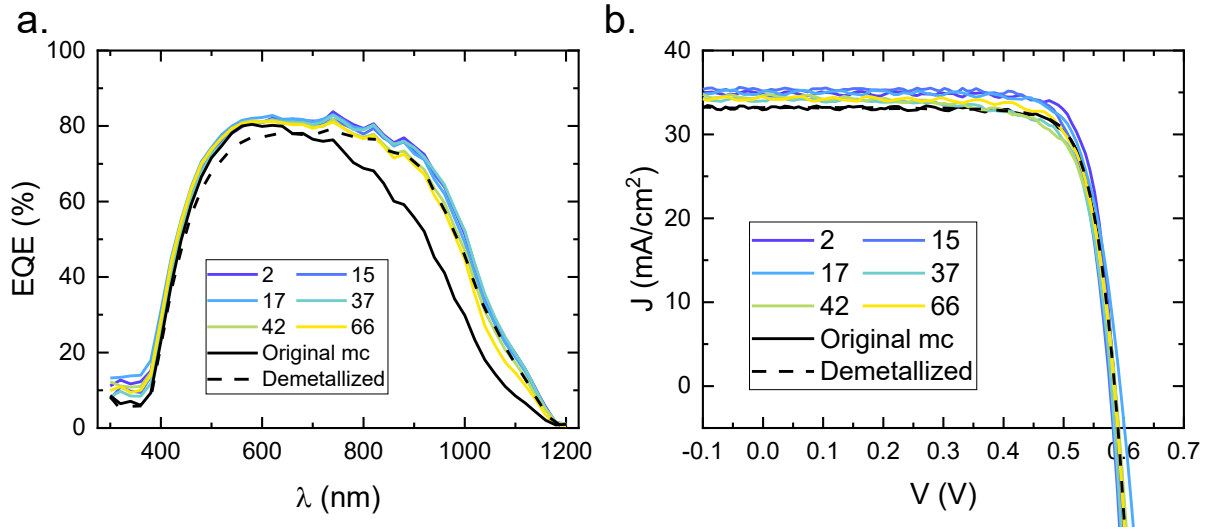

***Figure 5.** (a) EQE measurements for selected solar cells on recrystallized samples (coloured traces), on an original multicrystalline sample (black straight trace) and on a demetallized fragment (black dashed trace); and (b) corresponding I-V characteristics at 1 sun.*

As it can be seen, the EQE values for the recrystallized samples show a clear improvement from the multicrystalline devices, both demetallized and original. Numerical values extracted from the IV characteristics in Figure 7b, show that while V_{oc} values are in general pretty similar among all samples, all recrystallized samples present better J_{sc} figures than the reference sample, resulting in four out of six recrystallized samples showing better efficiency val-

ues, up to a 1.3% improvement. Also, the demetallized fragment and the multicrystalline reference present very similar efficiency values. This is a good indicator that there is no significant degradation during the demetallization stage.

From these results, it can be concluded that, while limitations are observed in the performance of the solar cells manufactured, they cannot be attributed to material degradation during the demetallization or recrystallization process; but rather to pitfalls during the solar cell manufacturing. As it can be seen in the EQE measurements, the backside of the solar cells shows poor performance, which can be ascribed to poor back surface field (BSF) performance.

Our findings suggest that the primary performance constraints observed in devices derived from recrystallized material and demetallized wafer fragments are not ascribed to material quality deterioration possibly incurred during the recovery and reuse phases of the silicon substrates. Rather, they stem from pitfalls encountered during cell manufacturing, notably highlighted by subpar BSF performance discerned in QE assessments and inadequate edge definition in the photolithography stage for front contact provisioning.

5. Conclusions

The effectiveness of demetallization and recrystallization processes in order to recover metallic species and reuse silicon substrates from decommissioned solar cells has been proven.

Alkaline treatments were optimized following a careful design-of-experiments process, allowing for complement removal and recovery of metals from front and rear contacts without damaging the quality of the demetallized substrates.

Monocrystalline wafers were grown from silicon fragments of old multicrystalline wafers, showing improvements in lifetime values after a PDG conditioning process, rendering them compatible with high-efficiency solar cell architectures and proving the feasibility of changing crystalline structure to adhere to the new trends appearing in the PV industry.

P/Al-BSF solar cells were manufactured, with devices on top of recrystallized substrates improving the optoelectronic characterization parameters of the original multicrystalline and the demetallized ones, assuring thus that no degradation of the material occurs during neither the demetallization nor the recrystallization and posterior processing.

These first steps towards the recycling of silicon solar cells support the idea that routes for the recovery and reutilization of their most valuable elements are technologically viable, and its establishment would lead the PV industry as a good example of circular economy.

Data availability statement

Data supporting the results of this article can be find in https://zenodo.org/communities/resiliens.

Author contributions

Dasilva-Villanueva N.: Conceptualization, Formal Analysis, Investigation, Methodology, Software, Writing – original draft, Writing – review & editing.

Caballero L.J.: Conceptualization, Data Curation, Methodology, Formal Analysis, Investigation, Methodology, Writing – review & editing.

Fuertes Marrón D.: Conceptualization, Formal Analysis, Methodology, Investigation, Supervision, Funding acquisition, Writing - Reviewing and Editing.

Rodríguez A.: Conceptualization, Methodology, Investigation, Supervision, Funding acquisition, Writing – original draft, Writing - Reviewing and Editing.

Díez E.: Conceptualization, Methodology, Data Curation, Investigation, Supervision, Funding acquisition, Writing – original draft, Writing - Reviewing and Editing.

Muñoz J.A.: Conceptualization, Methodology, Formal Analysis, Investigation, Supervision, Funding acquisition, Validation, Writing - Reviewing and Editing.

Braña A.F.: Conceptualization, Methodology, Investigation, Formal Analysis, Software, Supervision, Funding acquisition, Writing - Reviewing and Editing.

Plaza Canga-Argüelles J.L.: Methodology, Investigation, Supervision, Funding acquisition, Writing - Reviewing and Editing.

Cánovas E.: Conceptualization, Methodology, Supervision, Funding acquisition, Project administration, Writing - Reviewing and Editing.

del Cañizo C.: Conceptualization, Methodology, Investigation, Supervision, Funding acquisition, Project administration, Writing - Reviewing and Editing.

Competing interests

The authors declare that they have no competing interests.

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