An integrated thermal and hydrometallurgical process for the recovery of Silicon and Silver from end-of-life crystalline Si photovoltaic panels

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In the "2050 long-term strategy on adaptation to climate change", EU adopted measures to achieve the transformation towards a low-carbon economy, such as the replacement of fossil fuels by renewable energy resources by 30% by 2030. The use of solar energy, which represents a significant percentage of renewable resources, will increase over the next two decades by more than 40 GW/year (Yang et al, 2017). Europe holds the highest installed capacity, 70% of the total worldwide. Since 2012, photovoltaic (PV) panels are classified as WEEE, which require dedicated treatment at their End of Life (EoL). The quantity of the already installed PV panels and the expected growth lead to estimations of about 9.5 million tonnes of PV wastes by 2050 (Deng et al, 2019; Huang et al, 2017).

The significant amounts to be produced in the coming years, the potential environmental impact, mainly related to the leaching of heavy metals, and the potential benefit from the recovery of precious (Ag), rare (In, Ge, Ga, Te) and energy-intensive metals (Si) of high purity (>99.9%), are main reasons for the development of sustainable and environmentally friendly management practices and technologies (Dias et al, 2016; Yang et al., 2017). The recovery of high purity silicon and of other valuable metals is expected to result in materials saving and significant reduction of energy consumption and carbon emissions.

The present research work focuses on the development of an integrated process for the recovery of pure crystalline Si and electrowon Ag from EoL crystalline Si photovoltaic panels (SiPV), consisting of a primary thermal treatment of the Si modules, followed by a hydrometallurgical downstream recovery approach. The proposed process comprises the following seven (7) unit operations:

(1) Shredding the SiPV modules to -4 mm, after the removal and recovery of aluminium frames, junction boxes and copper cables.
(2) Delamination of the Si wafers from the front soda-lime protective glass, through a thermal treatment at 550 °C for 15 min, in excess of air, in order to disintegrate the encapsulating organic material (ethylene vinyl acetate (EVA)) and the polyvinyl fluoride (PVF) polymer backsheet (Tedlar).
(3) Separation and classification of the detached Si flakes from the front glass and the "ash residue", through mechanical screening, using a special designed perforated trommel rotary screen, equipped with square wire mesh sieves.
(4) Further grinding of the recovered Si flakes by ball milling to -90 μm, in order to increase the specific surface area, prior to the hydrometallurgical downstream process.
(5) Etching and recovery of silver and aluminium electrodes from the Si flakes, through acid leaching using 3N HNO_3, at ambient temperature.
(6) Further cleaning of the leached Si flakes, by 3N NaOH, in order to remove the anti-reflection coating (silicon nitride), targeting to the recovery of high-purity crystalline silicon, with almost identical quality to that produced for the initial fabrication of PV modules.
(7) Silver electrowinning from nitrate solutions (at 38 °C) using titanium plate as cathode and graphite rod as anode. The electrolyte concentration was fixed at 5 g/1 (pH=1), while the current density was kept constant at 90 A/m^2. The presence of Al did not affect the produced silver cathodes, as its reduction potential is too negative to allow its recovery by electrowinning from aqueous solutions.

The experimental results obtained from the leaching tests with 3N HNO_3 for silver recovery are shown in Fig. 1 for both Si flakes and powder from Si flakes ground by ball milling to -90 μm. Silver recovery is quantitative for both materials within 2 hours. For the ground samples, silver is leached by 80% within 0.5 hour upon contact with the leaching medium. According to the micrographs of Fig. 2, both Ag and Al are completely removed, leaving the etched silicon surface (Fig. 2c) free of metallic impurities.

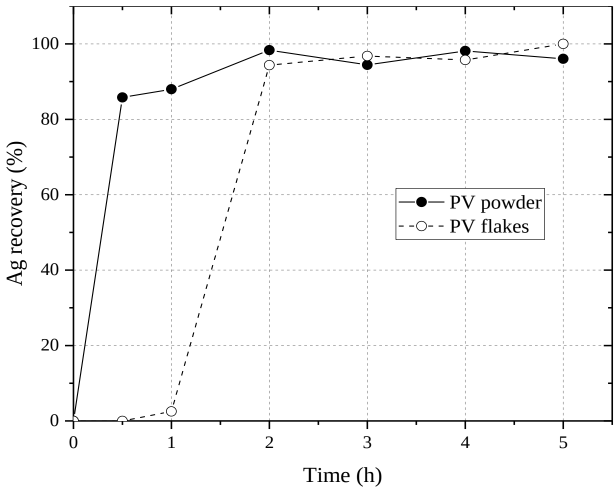
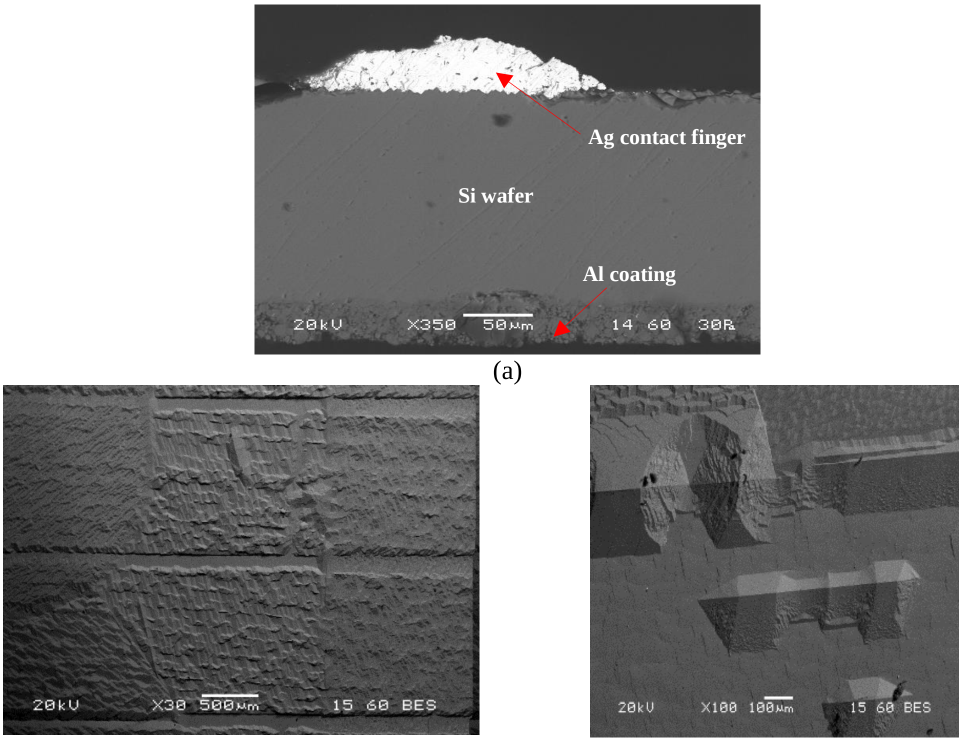


Fig. 1. Silver recovery from PV powder and flakes after leaching with 3N HNO_3 solution at ambient temperature



(a)

(b) (c)

Fig. 2. SEM micrographs of PV flakes (a) before and (b) after etching with 3N HNO_3 solution at ambient temperature and (c) etched silicon surface

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