Summary

In recent decades, there has been a significant surge in global energy demand, presenting challenges in sustainability and the environment. Renewable energy technologies, such as solar, wind, hydroelectric, and geothermal power, provide sustainable alternatives to fossil fuels with lower carbon emissions. Photovoltaic (PV) technology, which directly converts solar energy into electricity, has seen recent advances that offer higher efficiency and versatility. With the expected exponential increase in installed PV capacity in the coming decade, challenges such as material scarcity and efficiency become increasingly important.

This thesis focuses on replacing indium tin oxide (ITO) with metal nanowire networks (MNNs) as transparent conducting materials (TCMs) for PV applications. MNNs have gained attention due to their excellent electrical conductivity, mechanical flexibility, and potential for tailored optical properties. One crucial aspect in TCMs is striking a balance between electrical conductivity and optical transparency, measured by the Figure of Merit (FoM). The design flexibility of MNNs allows for precise control over optical behaviour, making them highly suitable for light management in PV devices.

In this thesis, we propose the combination of electrodeposition with nanoimprint lithography, as it offers a sustainable and scalable approach for producing well-defined MNNs with precise control over size, shape, and alignment. As demonstrated, this method enables efficient material usage, reducing the overall amount of silver required for manufacturing while maintaining high performance. The development of such materials and methods contributes to a more sustainable solar energy infrastructure, aligning with global efforts towards a cleaner, renewable energy future.

In Chapter 2 we gave a brief introduction to electrochemical theory, describing the definition of an electrochemical reaction, discussed the importance of thermodynamics, electrode kinetics, and mass transport, and described the most commonly used electrochemical techniques. We then focus on the electrochemical deposition of metals on foreign substrates and discussed the importance of the current density distribution on the uniformity of the deposit. We also described a finite element method to simulate the spatial-temporal electrochemical response in 2D electrodes, including cyclic voltammetry and chronoamperometry. From our simulations, we found that cyclic voltammogram simulations of electrodes with a roughness in the order of microns are very sensitive to the tertiary current distribution determined by the concentration profile at the morphological features. Finally, we used our finite element simulation platform to model the chronoamperometry of the growth of metal in nanosized trenches, which is the main topic of this thesis. We showed that these nano-sized trenches can be simply modelled by 1D diffusion as the trench depth is much smaller compared to

the diffusion length.

In Chapter 3 we dived into the electrochemical nucleation of silver on foreign substrates, in particular ITO, using the double pulse technique. We have showed that ITO substrates with the same technical specifications (i.e., sheet resistance, light transmittance, and roughness) and supplier may still have a different crystalline texture, which we found it has a strong impact on the nucleation and growth of silver nanoparticles during electrodeposition. We found that the preferential presence of lower index surfaces leads to a few orders of magnitude lower island density, which strongly depends on the nucleation pulse potential. On the contrary, the island density on ITO with preferential <111> orientation is barely affected by the nucleation pulse potential. This chapter highlighted the importance of reporting the surface properties of polycrystalline substrates when presenting nucleation studies and metal nanoparticle electrochemical growth.

Next, in Chapter 4, we have combined the double pulse method with substrate conformal imprint lithography (SCIL) to fabricate silver nanowire (NW) grids on ITO substrates for the use as TCM for PV applications. The presented method is based on a through-the-mask electrodeposition method, where the mask is made using SCIL. We found that the nucleation density of the silver nanoparticles is the key parameter for the successful homogeneous void-free filling of the template. By using the obtained knowledge from Chapter 3, we independently controlled the density of the silver nuclei and their growth by using the double pulse technique. The silver NW grids show high optical transmission (95.9%) and low sheet resistance (as low as $3.7\ \Omega/\mathrm{sq}$), resulting in a superior Figure of Merit (FoM). Due to the bottom-up nature of this technique, arbitrarily high aspect ratio nanowires can be achieved and therefore decrease the sheet resistance without affecting transmittance and carrier collection.

Until now we had only discussed the average transmission of the silver NW grids. However, their nanophotonic nature in combination with the periodic spacing opens up new possibilities for light management by NW-based TCMs. Therefore, in Chapter 5 we have described the light-matter interactions of these silver NW grids. We have discussed the origin behind the characteristic spectral features in transmission and how are these affected by geometry and dielectric environment. We used FDTD simulations to predict light transmission and absorption by the grids, and we showed that the FDTD simulated data explained our experimental observations. Furthermore, the FDTD simulations validated the normalisation method used in Chapter 4 to decouple light transmission of the silver NW grids from that of the substrate in the experiments.

The second part of Chapter 5 described the use of in-situ bright field microscopy to monitor the nucleation and growth of the grid formation. We found that the silver nanoparticles strongly absorb light upon nucleation, resulting in a sudden decrease in reflectance, which is observed both in bright-field microscopy and in spectroscopy. As the nanoparticles grow larger and eventually coalesce, more light is scattered, which makes the grid pattern appear bright in the microscopy images.

Up until this point, we showed that the silver NW grids are highly transparent and conducting making them suitable for the usage of TCM in PV applications. In Chapter 6 we went one step further by integrating the silver NW grids into an actual solar cell device. We demonstrated the successful fabrication of silver NW grids directly grown on Si-based solar cells by electrochemical deposition without using a seed layer. We have used tunnel oxide passivated contact (TOPCon) solar cells as platform to measure the transparency of the silver NW grids in the right dielectric environment via short-circuit current density (J_{sc}) monitoring, and we showed that the transmission of the silver NW grids is greater than expected from their geometrical footprint. Moreover, we investigated the effect of nanowire aspect ratio on the angle-dependent J_{sc}. We found that the J_{sc} is virtually constant up to an angle of incidence of about 40°, after which the current drops. This decrease in current density at larger angles of incidence was attributed to the increase in absorption by the silver NW grids. Overall, this chapter showed the successful integration of the silver NW grids into real Si-based solar cells, and even improving the performance of the solar cell in the near-infrared spectral regime.

Finally, in Chapter 7, we investigated the use of monocrystalline silver nanocubes as seeds for the electrochemical growth of silver nanowire grids with potentially higher crystalline quality and thus better electrical performance. Nanocube imprint lithography developed by our collaborator was used to assemble colloidally-grown monocrystalline nanoparticles with a size of 40 nm into a grid-like pattern on ITO substrates. Subsequently, we focused on the welding of these silver nanocubes via electrochemical overgrowth. We took advantage from our knowledge obtained in Chapter 3, and used the large nucleation overpotential of silver on ITO substrate to selectively electrodeposit silver on the nanocubes without inducing the formation of new silver nuclei on the ITO substrate. We showed indirect evidence for epitaxial overgrowth, as the electrochemically-induced grain size increase in the nanocubes, as obtained from XRD, coincides with that from morphological measurements (AFM and SEM). Our findings also underscore the critical importance of ligand removal for the successful overgrowth and welding.

In general, in this thesis we have reported a scalable selective area electrochemical method for fabricating interconnected metal nanostructures for transparent conducting materials. Utilising the bottom-up approach of this technique allows for achieving arbitrarily high aspect ratio nanowires, thus reducing sheet resistance without compromising transmittance and carrier collection. This feature proves advantageous for integrating silver nanowire grids into TOPCon solar cells. As such, this thesis contributes to a more sustainable solar energy infrastructure, opening up new paths towards a cleaner, and more renewable energy future.