Transparent conducting materials: overview and recent results

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ABSTRACT

An overview of different transparent conductors is given. In addition, atmospheric pressure CVD of ZnO resulted in conductivities below 1 mΩ cm for a temperature of 480°C, whereas at a process temperature of 200°C a value of 2 mΩ cm was obtained. Also atmospheric pressure spatial ALD was used to make conductive ZnO. Furthermore, the properties of transparent conductive oxides (TCO) can be enhanced by application of metallic grids. This way, sheet resistances of below 0.1 Ω/sq and transmittances above 85 % can be achieved. Modeling indicates that the performance of thin film cells can be enhanced by18% using a grid/TCO combination. Light scattering is a vital element of thin film solar cells and both texturization and multimaterial approaches for advanced light management such as plasmonics are discussed.

Keywords: transparent conductors, transparent conducting oxides, metal grids, thin film solar cells, plasmonics

1. INTRODUCTION

A wide variety of transparent conductors in terms of new materials are becoming available that could serve as an alternative to ITO, which is commonly applied in displays. ITO is one of the best transparent conductors, but indium is quite expensive. Furthermore, ITO is deposited by sputtering process, a low pressure method, which requires substantial investment in equipment. Cheaper alternatives, such as fluor doped SnO_2 and aluminum doped ZnO (AZO) are the most widely used for thin film solar cells. In spite of their popularity, TCOs have some major drawbacks. For all TCOs, including SnO_2 and ZnO, the limited transparency in the infrared and the brittleness are the main concerns [1, 2]. As a result, alternatives for TCOs have been explored [2]. For example, thin metal sheets, graphene and carbon nanotubes can function as transparent conductors. However, it can be noted that for these materials layer thickness higher than a few nanometers or even monolayers reduces the transmittance dramatically, limiting the optoelectronic device output when these materials are used.

In R&D of transparent conductors, most efforts to get better performances have been devoted to improved material quality in terms of higher carrier mobility or more homogeneous distribution of the material, which is a challenge when high-rate, low-cost deposition methods are used. Doped zinc oxide (ZnO) films have received increasing interest in recent years since they combine the common properties of TCO, i.e. high conductivity and excellent transparency, with low cost, low toxicity, easy fabrication and patterning [3,4]. In particular, doped ZnO has become a valid alternative to the commonly used indium tin oxide (ITO) as TCO layer for silicon thin-film solar cells, being highly stable in a hydrogen plasma environment [5-7]. This work presents atmospheric pressure chemical vapor deposition of ZnO, in addition to our previous APCVD work on SnO_2.

Moreover, an alternative approach for better device performances is to use more than one material, the so-called multimaterial approach. In this work, TCOs were combined with metallic grids, applied by electrochemical deposition resulting in excellent conductivities with only a minor reduction of the transmittance. In order to evaluate the impact of such grid in a thin film PV device, the output of a thin film CIGS solar cells was modeled with various cell dimensions and TCO characteristics for TCO-only and TCO + grid front contacts.

An increasing part of TCO research is being devoted to light management, mainly focused on scattering light at the TCO/PV absorber interface. In addition, new light management schemes such as plasmonics have recently come up and this work presents some results on the combination of TCO and nanoparticles.

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2. RESULTS

2.1 Transparent conducting oxides

A typical wavelength distribution of the transparency of TCOs is shown in figure 1.

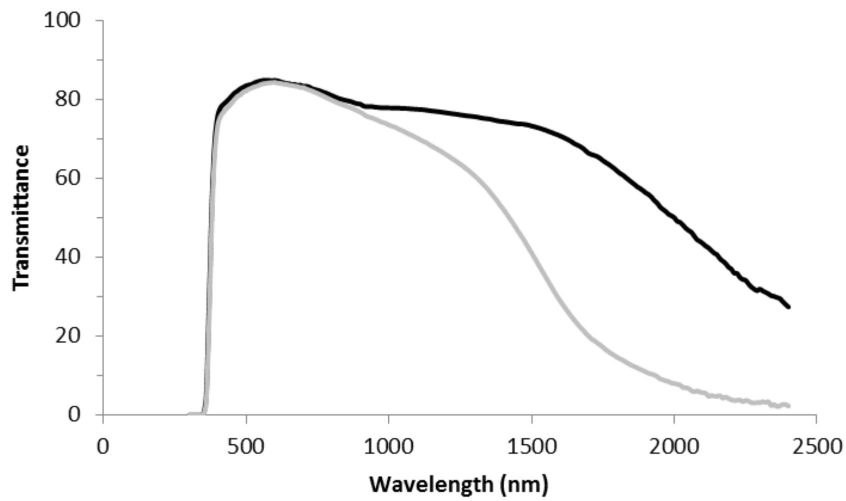

Figure 1. Transmittance as function of the wavelength of a SnO_2:F with a carrier concentration of 1×10^{20} cm^{-3} (black line) and a carrier concentration of 4×10^{20} cm^{-3} (grey line) as produced with atmospheric pressure chemical vapor deposition (APCVD).

As can be seen, the transmittance decreases at higher wavelengths and also decreases with an increase in carrier concentration. Although metal oxides are known for their reflectance in the infrared (which is why they are used in low-e glass) the reduced transmittance presented in fig. 1 is mainly due to absorption. The relation between free carrier absorption A_{fc}, wavelength of light and carrier concentration N can be described by the equation [8]

$$A_{fc} = \frac{\lambda^2 e \ Nt}{4\pi^2 \varepsilon_0 c^3 nm^{*2} \ \mu} \tag{1}$$

With λ is wavelength, e electron charge, t is layer thickness, ε_0 is dielectric constant of free space, c is the velocity of light, n is the index of refraction, m^* is the electron effective mass and μ is the mobility. For indium oxide related materials, it was reported that transmittance loss due to absorption becomes significant at a carrier concentration of about 10^{21} cm^{-3} [3]. However, fig. 1 shows that already for a carrier concentrations of 4×10^{20} cm^{-3} , the wavelength range in which absorption takes place approaches 1100 nm and, therefore, becomes relevant for thin film solar applications. Equation 1 shows that the absorption scales linear with carrier concentration. Also, it is considered inversely proportional to the free carrier mobility. In other words, conductivity and transmittance can be simultaneously increased by a higher mobility and has resulted in considerable efforts devoted to increase of the mobility and promising materials like cadmium oxide [9]. However, although CdO has a very high mobility, its band gap of 2.2 eV limits its applicability in PV [10]. Moreover, cadmium related materials have the drawback of environmental concerns. For this reason our TCO work focused on the low hazard and abundant material of ZnO.

2.2 ZnO deposition

Several deposition techniques are used for the growth of ZnO, as: sputtering, pulsed laser deposition, solution process methods, APCVD, plasma-enhanced chemical-vapor-deposition (PE-CVD) and atomic-layer-deposition (ALD) [11 - 14]. An APCVD process was developed with ZnO:Al layers having a conductivity as low as 0.5 mΩ cm and a transmittance above 80% [12]. This type of layers was used for deposition of a-Si solar cells, resulting in an efficiency of approximately 8%. Furthermore, it was observed that the transmittance shows a steep drop above 1100 nm due to free carrier absorption [12], while in figure 1 a much more smoother decline with wavelength was shown for SnO_2:F. It is unclear why the spectral distribution of the free carrier absorption is different in this way. The APCVD process of ZnO has a deposition rate of 14 nm/s with a single injector under which the sample is passed. This dynamic deposition method allows for multiple passes of the substrate underneath a fixed injector. This way multilayers have been made and with approximately 450 nm layer thickness for each pass. Moreover, it was found that the full width half maximum of the (002) XRD peak declined more than with single layers, indicating a higher crystalline quality [11]. Indeed, crystal sizes increased and R_{ms} values of 12 nm, 25 nm and 32 nm were obtained for single, double and triple passes, respectively.

Spatial ALD combines the advantages of the conventional ALD, i.e., growth of uniform, pin-hole free and highly conformal thin films on large area and flexible substrates, with high deposition rates (~ nm/s) [15]. For this reason, spatial ALD has been proposed as an innovative technique for the growth of thin films in the electronics and solar cells industry. The electrical properties of the ZnO films, ranging from heavily n-type conductive (with 4 mΩ cm resistivity for 250 nm thickness) to insulating are controlled by a variation of the partial pressure of the zinc precursor, i.e. diethylzinc (DEZ) [14]. The optical properties of the ZnO films have been investigated by means of spectrophotometer. The transmittance as function of the wavelength of ZnO is shown Figure 2. ZnO films exhibit high optical transmittance, reaching a mean value of above 85 % in the visible range. Using the standard $(\alpha h\nu h)^2 \sim (h\nu\text{-}Eg)$ relation, we calculated the optical band energy (Eg), which is found to have a systematic blue shift with increasing carrier concentration (N), according to the relation ($Eg \sim N^{2/3}$), consistently with the Burstein-Moss model.

Combining the control of defects-related functional properties (i.e. conductivity and transparency) of ZnO with high growth rate, the industrially scalable spatial-ALD technique has the potential of becoming a manufacturing method for the ZnO based industry with nm thickness resolution

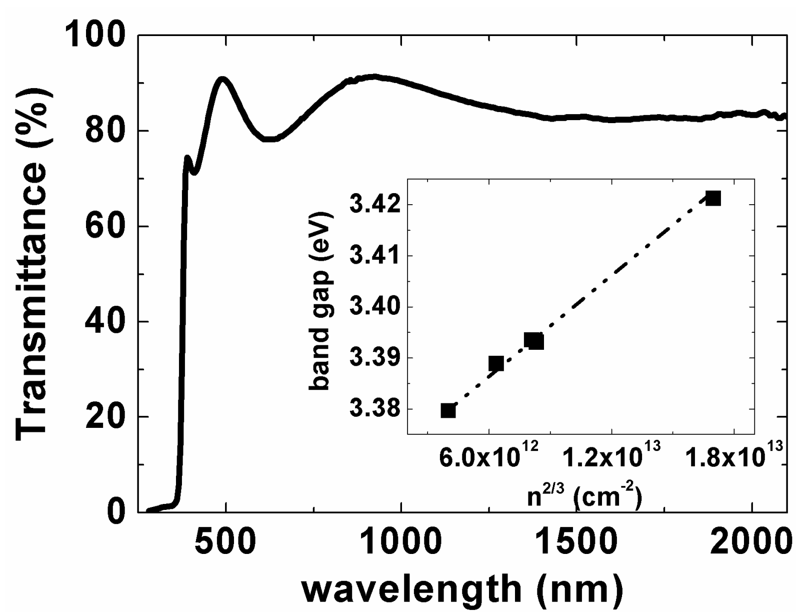

Figure 2 Transmittance spectrum of ZnO film deposited at 250 °C and a DEZ partial pressure of 4.58 mbar. Inset: band gap as a function of carrier concentration.

2.3 Transparent conducting materials

As TCOs have drawbacks of brittleness, alternative materials have come up and figure 3 displays a comparison of three different classes of materials: TCOs, thin metal films and carbon nanotubes.

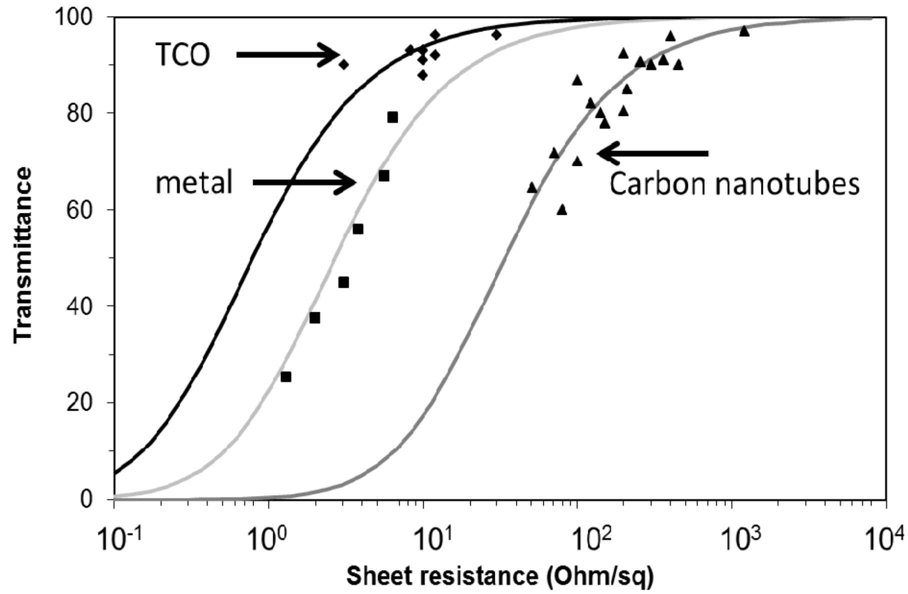

Figure 3. Transmittance as function of the sheet resistance of various transparent conductors. The lines are according to equation (2) as described in the text.

For equivalent sheet resistances, the transmittances of TCOs are higher than for the other materials presented in figure 3. Metal films can obtain low sheet resistances, but only at a much lower transmittance than obtained for TCOs. For evaporated thin metal films, it usually requires a few nanometers for the layer to be coherent [16]. Metal films of more than a few nanometers, often have low transmittance. Carbon nanotubes are very interesting, but up to now, the performance is much lower than for other materials available. Figure 3 shows that the maximum transmittance versus sheet resistance values of transparent conductors follow the same trend of transparency (T) versus the sheet resistance (R_s), which can be quantified by a rather simple equation containing the ratio of the optical conductivity σ_{op} and the dc conductivity σ_{DC} [3]

$$T = \left(1 + \frac{1}{2R_s}\sqrt{\frac{\mu_0}{\varepsilon_0}}\frac{\sigma_{op}}{\sigma_{dc}}\right)^{-2} = \left(1 + \frac{188(\Omega)}{R_s}\frac{\sigma_{op}}{\sigma_{DC}}\right)^{-2} \quad (2)$$

In which the free space permeability $\mu 0 = 4\pi \times 10^{-7}$ s^2/Fm and permittivity $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m. For thin film solar cells, transparent conductors are needed to remove the generated current from the top side. High transmittance is needed for high light influx, while a high conductivity is required to prevent ohmic losses. As can be seen from equation 2, there is a trade-off between transparency and sheet resistance (see also figure 3) and for each application the specific demands will determine the best material to use and with which specific material characteristic.

2.4 Multimaterial transparent conductors

To overcome the limits of the single material solutions shown above, metal grids were deposited on top of a commercial TCO. Results presented here are based on lithography based patterning, but we have also demonstrated large scale compatible patterning, such as micro contact imprint and laser texturing. These methods do not require a mask and enable selective deposition of the metal. Figure 4 shows the transmittance as function of the sheet resistance of TCOs and a commercial ITO on PET supplied with a metallic grid.

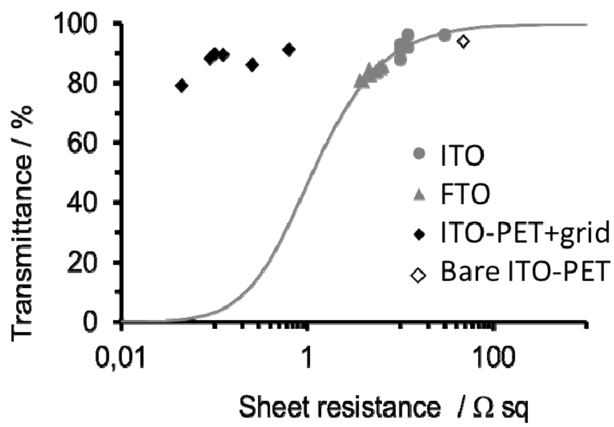

Figure 4. Transmittance as function of the sheet resistance of indium tin oxide (ITO), fluor doped tin oxide (FTO), a commercial ITO sample on PET foil (ITO-PET) with and without a metallic grid. The various sheet resistances represent various grid designs and layer thicknesses of the deposited metal and the line corresponds to the TCO line in the figure above.

Starting with a transmission of above 90% and a sheet resistance of 45 Ω/sq for bare ITO on PET (excluding the influence of the substrate), the sheet resistances in the range of 0.1 Ω/sq have been achieved at transmittance losses of only a few percent. Further reduction of the sheet resistance towards 0.01 Ω/sq require higher surface coverages above 10%. This leads to considerable transmittance losses as represented by the data point on the far left. These results are a great step forward compared to reported work on single material transparent conductors and demonstrate that by combining TCOs and metals, the physical boundaries of each individual material can be overcome.

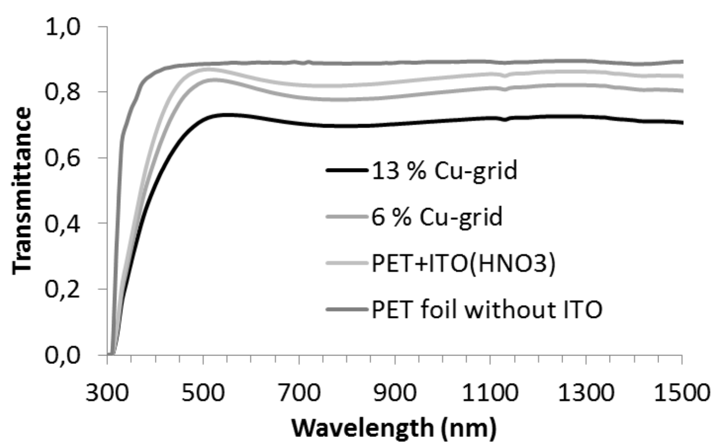

Figure 5. Transmittance as function of the wavelength of commercial ITO on PET foil (PET+ITO),with and without a metallic grid with surface coverages of 6% and 13% and the PET foil with the ITO removed as to visualize the base line.

The transmittance values are an average between 400 nm and 800 nm. A more detailed analysis of the transmittance is shown in figure 5. The grid with a surface coverage of 13%, gave rise to a transmittance loss of about 13%, as expected. However, the surface coverage of 6% the transmittance loss was only 4%. This demonstrates that the use of narrow lines have a benefit. And more investigation is needed to explore the potential of creating highly transparent grids.

Modeling for the thin film PV case resulted in optimized grid and cell dimensions [17]. An optimum line width of 20 μm was calculated and this was used as a starting point of the grids produced. More importantly, modeling results indicated that by taking an IV curve of a commercial CIGS cell of 11,7% based on a bare TCO of 10 Ω/sq, the efficiency could be enhanced up to 13,8% when applying a grid with optimized TCO characteristics (100 Ω/sq for the TCO) and a surface coverage of 2%. Previously, similar jumps in efficiency have been reported for modules [18]. It should be noted, that for thin film PV, the optimum grid design was built up out of parallel lines, but that in the present study a grid was used for general purposes and consists of perpendicular lines, which make squares.

2.5 Research directions of advanced light management for thin film PV.

Multimaterial combinations have resulted in improved conductivities. Furthermore, for PV applications, there is also a growing need for thinner photoactive layers and this development requires light management. Up to now texturing of TCOs have increased the performance of thin film cells by elongating the pathway of light through the PV absorber material and example structures as obtained with APCVD of SnO_2:F are shown in figure 6. These structures scatter the light and reduce reflection. However, for further reduction of the active layer more advanced light management techniques are required. Again, multimaterial structures can contribute to achieve such goals [19, 20].

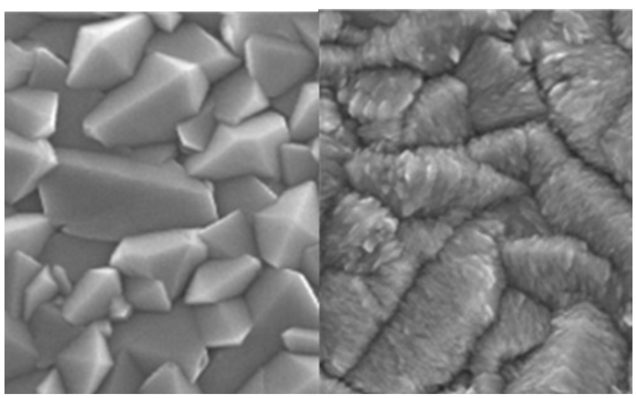

Figure 6. Example structures of SnO_2:F as deposited with APCVD. The width of each image is approximately 1 micron.

Metal nanoparticles on top of a dielectric material can result in interesting light incoupling behavior [19]. Figure 7 shows a helium ion microscope image of silver nano particles on top of ZnO. These nano particles were formed by annealing a14 nm Ag film deposited on a ZnO layer, which was made by APCVD. The annealing causes the Ag to form small sphere-like structures. As both methods are used for large area coating, this opens the way for nanotechnology on the square km scale, without the need for masks or printing steps. As ZnO is a part of many thin film solar cell configurations, the combination of Ag and ZnO seems a valid approach for light management. To get an indication of the possible effects, the reflectance and absorption of the sample shown in figure 7 are presented in figure 8. Clearly, the absorption peak refers to the plasmon resonance. Such resonance can be preferably scattered into the solar cell material and the benefit of a thin dielectrical layer in between the nanoparticle and the solar cell material has already been reported [20]. More advanced light management can be obtained by nano imprint lithography, up and down conversion but the true applicability in terms of effectiveness and robust producibility still has to be demonstrated.

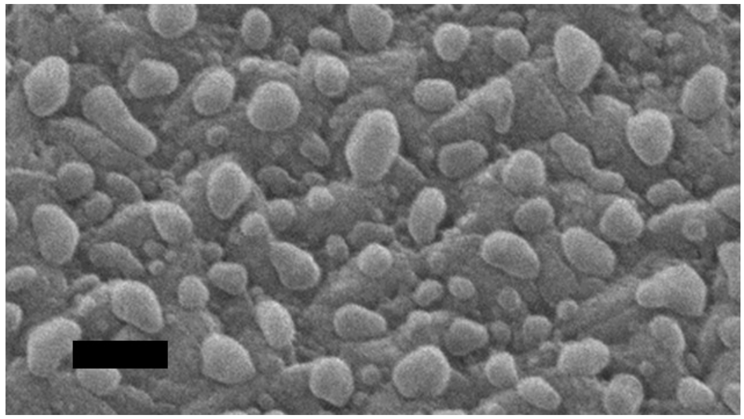

Figure 7. Helium ion microscope image of annealed Ag on top of microcrystalline ZnO. The scale bar represents 50 nm.

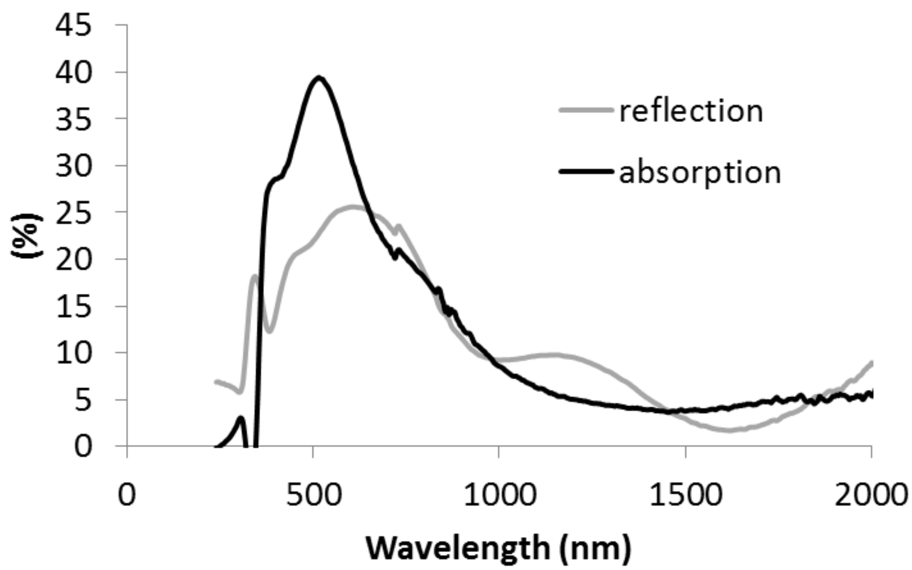

Figure 8. Reflection and absorption of annealed Ag on top of ZnO.

3. CONCLUSIONS

Transparent conductors have a trade-off between conductivity and transparency. For single materials, TCOs are still among the best options and patterned metal-TCO multimaterials have been developed to overcome the barriers of single materials, resulting in sheet resistances below 0.1 Ω/sq, while maintaining a high transparency. Conductive ZnO has been deposited with APCVD and ALD. For APCVD samples with a native texture, an a-Si cell of 8% was obtained without optimization. Optical characterization of ZnO showed a blue shift with increasing carrier concentration consistent with the Burnstein Moss model. In addition to light management by textured TCOs, preliminary data on optical characteristics of metal nanoparticles on TCOs show intense absorption and more work on this topic will be pursued.

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