Amorphous ZnO Films Grown by Room Temperature Pulsed Laser Deposition on Paper and Mylar for Transparent Electronics Applications

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ABSTRACT

Recently, there has been a surge of activity in the development of next-generation transparent thin film transistors for use in applications such as electronic paper and flexible organic light emitting diode panels. Amongst the transparent conducting oxides attracting the most interest at present are Amorphous Oxide Semiconductors (AOS) based on ZnO because they exhibit enhanced electron mobility (μ), superior capacity for processability in air and improved thermodynamic stability compared with conventional covalent amorphous semiconductors and existing AOS. Moreover, they give excellent performance when fabricated at relatively low temperature and can readily be made in large area format. Thus, they are projected to resolve the trade-off between processing temperature and device performance and thereby allow fabrication on inexpensive heat-sensitive substrates. For the moment, however, an undesireable post-deposition annealing step at a temperature of about 200ºC is necessary in order to obtain suitable electrical and optical properties. This paper demonstrates the possibility of directly engineering amorphous ZnO with relatively high conductiviy at room temperature on paper and mylar substrates using pulsed laser deposition.

Keywords: ZnO, Room Temperature Pulsed Laser Deposition, Paper Substrate, Mylar Substrate, Transparent Electronics, Transparent Conducting Oxide, Thin Film Transistor, Amorphous Oxide Semiconductors

1. INTRODUCTION

Wurtzite ZnO is a remarkable multifunctional material with a distinctive property set and a huge range of existing and emerging applications [1]. In particular, it is a direct wide bandgap semiconductor (Eg ~ 3.4eV) with intrinsically high transparency over the whole visible range (Fig. 1) and a resistivity that can be tuned from semi-insulating right through to semi-metallic by doping [2].
In the latter case, ZnO can be considered as belonging to a class of materials termed "Transparent Conducting Oxides" (TCO). TCOs are degenerate n-type semiconductors

with resistivities under about 10^{-3} ohm.cm, free-electron concentrations of the order of 10^{20} cm^{-3}, an Eg > 3.1 eV and average transmittance > 80% for the whole visible range.

Although many new TCO materials have been developed in recent years, most practical TCO applications employ doped oxides of Indium, Tin and Zn. These are passive applications including window defrosting, filtering of ultra-violet and/or infra-red light, electromagnetic shielding, transparent wiring, touch-sensitive panels and transparent contacts for use in flat panel displays, solar cells and light emitting diodes [3]. Most of these applications need as conductive and transparent a TCO as possible.

Recently, a new kind of ZnO-based TCO has emerged. These are Amorphous Oxide Semiconductors (AOS) [4]. Compared to wurtzite ZnO, amorphous ZnO-based alloys have lower processing temperatures, are cheaper to fabricate, are lighter and have better uniformity of properties (due, in part, to a lack of grain-boundary-related issues). Moreover, their performance is stable and reproducible during and after repetitive bending, so they are compatibility with flexible substrates.

Although AOS are not a new class of materials [5] the new generation of ZnO-based AOS exhibits enhanced electron mobility (μ), superior capacity for processability in air and improved thermodynamic stability compared with conventional Covalent Amorphous Semiconductors (CAS) and existing AOS [6].

Nomura et al. [6] proposed, that the improved μ are obtained because of differences in the intrinsic nature of the chemical bonding between AOS and CAS. In CAS the hybridized sp3 orbital overlap is highly directive. Therefore, any bond angle fluctuations significantly alter the electronic levels, and carrier transport is thus controlled by hopping between localized tail-states rather than band conduction. Hence structural randomness can greatly degrade the carrier mobility. AOS, in contrast, have higher ionicity and the bottom of the conduction band has extended, spherical s orbitals associated with the metal ion. These electronic levels have an overlap which is relatively insensitive to distortion of the metal–oxygen–metal chemical bonds. Thus strain and disorder within the material do not strongly impact the conduction such that AOS materials can show degenerate band conduction and superior electron μ compared with CAS, even though they are formed at Room Temperature (RT). Indeed, amorphous InGaZnO$_4$ (a-IGZO) [7], can have a Hall μ > 12cm^2/Vs [8] compared with a typical μ of < 1 cm^2/Vs for hydrogenated amorphous Si (a-Si) and it is reported to be stable up to 500°C in air [6]. Amorphous InZnO (a-IZO) can have even higher μ (> 100cm^2/Vs: [9]) plus a transparency and conductivity which are comparable with ITO [10]. As such, it is an alternative material for electrode applications. It shows inferior control of carrier concentrations compared with a-IGZO, however, so a-IGZO is preferred for use as the channel [11].

Although ZnO based TTFTs are not a new concept [12,13], the new generation exhibits a high on-off ratio (>10^6) and a higher channel μ than the Si based devices which are currently used for state-of-the-art microelectronics applications such as select transistor drivers in commercial liquid crystal displays and systems-on-glass. Two main ZnO TTFT variants, employing either wurtzite or AOS ZnO alloys as channels, have emerged [6, 14-18].

These ZnO-based TTFTs offer several advantages over the incumbent Si based devices. First of all, they are transparent, so that generally more light can be transmitted through

each pixel, yielding a brighter, more efficient, display. This also means that the aperture ratio can be increased, so as to give smaller pixels. Next, state-of-the-art wurtzite ZnO and a-IGZO TTFTs can now exhibit channel μ as good as $250cm^2/Vs$ and $12cm^2/Vs$, respectively, as compared with typical values of $100cm^2/Vs$ and $1cm^2/Vs$ for poly-Si and a-Si [19]. This gives faster device operation, which leads to a quicker response and an increased refresh rate. In addition, because of their wide bandgap, the ZnO based TTFTs have reduced sensitivity to light (exposure to ambient light has no significant effect on the current–voltage characteristics) and less degradation on exposure to light compared with their a-Si counterparts. TTFTs made with a-IGZO are of particular significance because they give excellent performance when fabricated at RT and can be fabricated in large area format. This is often touted as resolving the trade-off between processing temperature and device performance so as to allow fabrication on inexpensive heat-sensitive substrates such as transparent polymers or paper (poly-Si deposition temperature is too high for many flexible polymer substrates). For the moment, however, an undesireable post-deposition annealing step at a temperature of about 200ºC is necessary in order to obtain suitable electrical and optical properties.

In this paper, we examine the possibility of avoiding such an annealing step through the use of Pulsed Laser Deposition (PLD) to engineer amorphous ZnO with good electrical and optical properties at RT. PLD has already shown potential for the fabrication of TFTs with wurtzite ZnO channels for operation with high device currents/powers and/or high frequencies [20]. Indeed, PLD has the capacity to grow wurtzite ZnO with superior crystallographic quality, a very large range of conductivities and excellent optical quality compared with other deposition techniques [21]. This is due to intrinsic advantages of PLD including the relatively high energy of the species in the ablation plume (~10 to 100eV in PLD vs ~ 1 to 10eV for sputtering and 0.1 to 1 eV for MBE or CVD) and the extended range of oxygen partial pressures under which films can be grown (Fig. 1).
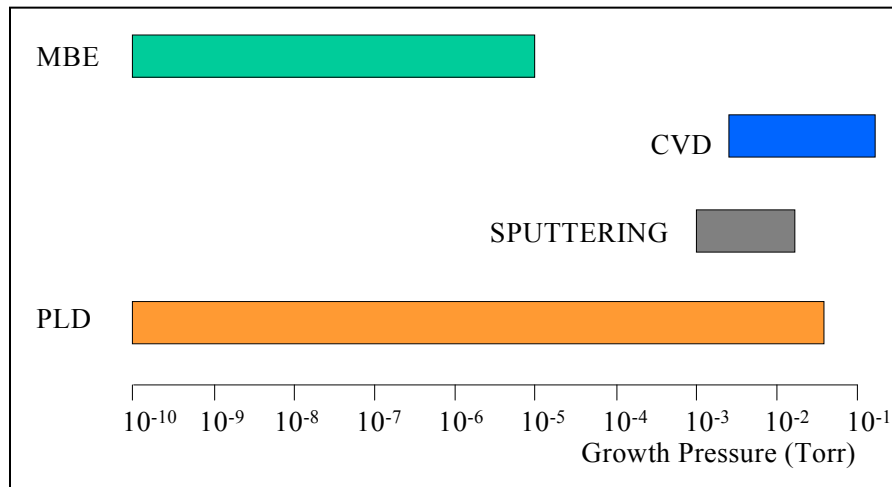

Figure 1. A comparison of typical dynamic operating pressure ranges for common thin film deposition techniques.

The combination of these features allows a great flexibility for tuning of the oxygen content over a very large range, of oxidant (or reducing gas) partial pressures plus the capacity to form wurtzite ZnO at temperatures down to RT.

To date, however, there have been very few studies into the fabrication of AOS ZnO by PLD. This is because ZnO tends to crystallize after a few nm of deposition, even at RT on amorphous substrates (e.g. glass [22]) under typical PLD conditions.

In this study the aim was to investigate the potential of PLD for the synthesis of conductive amorphous ZnO layers adapted for transparent electronics applications on heat-sensitive substrates.

2. EXPERIMENT

ZnO layers were deposited on (standard photocopy) paper and mylar (polymer) substrates held at RT by ablation of a 5N ZnO target with a KrF (248 nm) excimer laser. The sample morphology was studied using a Hitachi S4800 field emission-Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-Ray (EDX) spectroscopy for compositional microanalysis. X-ray diffraction (XRD) studies were conducted with a High Resolution (HR) 4-circle Philips X-Pert MRD PRO system using Cu Kα radiation. Resistance measurements were made for injection currents of 0.01, 0.1 and 1 mA using an aligned 4-point measurement system with a Keithley 2400 source-meter. Optical properties were studied using Ultraviolet (UV) RT photoluminescence (PL) spectroscopy with a HeCd laser emitting at 325 nm.

3. RESULTS & DISCUSSION

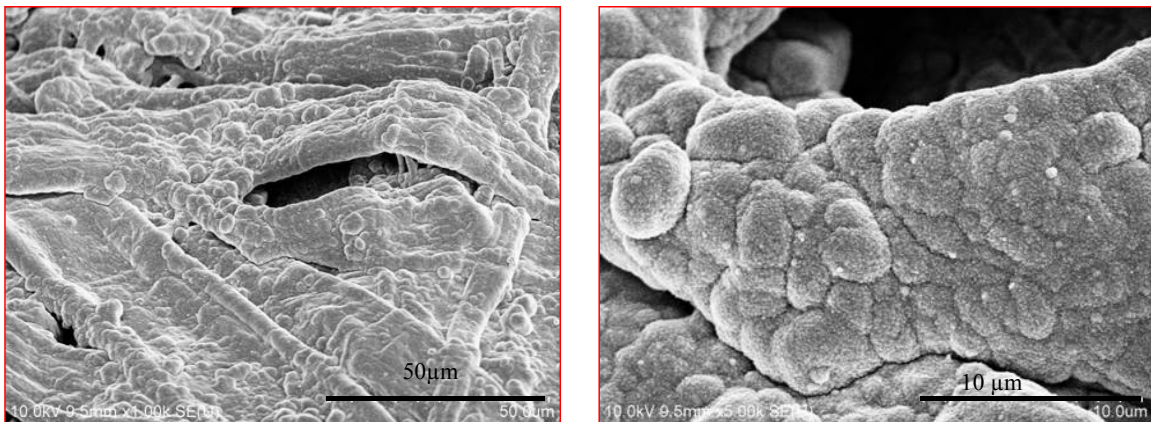Figure 2 shows SEM images for the ZnO/paper.

Figure 2. SEM images for ZnO deposited on paper using RT PLD.

The SEM studies showed the cellulose fibres of the paper but no evidence of a crystalline coating was observed. Figure 3 shows SEM images for the ZnO/mylar
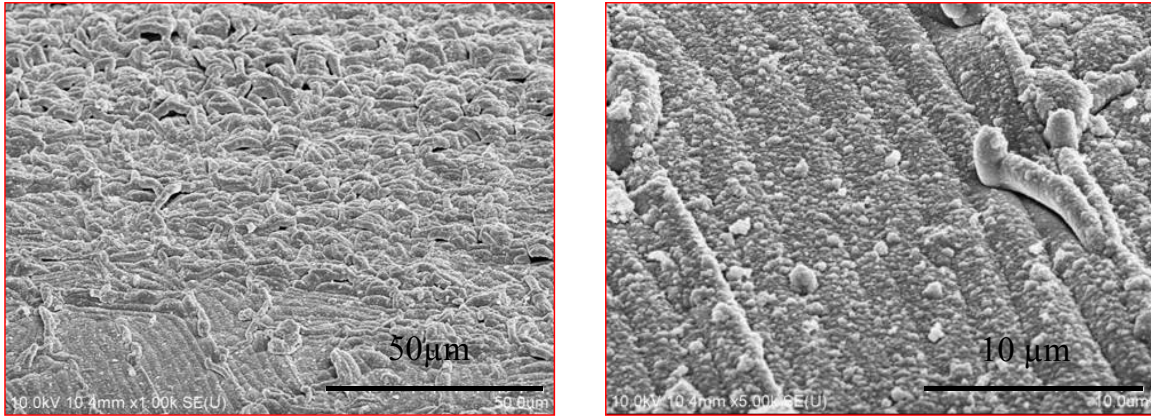
Figure 3. SEM images for ZnO deposited on mylar using RT PLD.

The SEM images show structure typical for a polymer substrate with no evidence of a crystalline coating.

EDX spectroscopy was conducted for the ZnO/paper and ZnO/mylar in order to verify the presence of a ZnO layer. A typical spectrum is shown in figure 4.
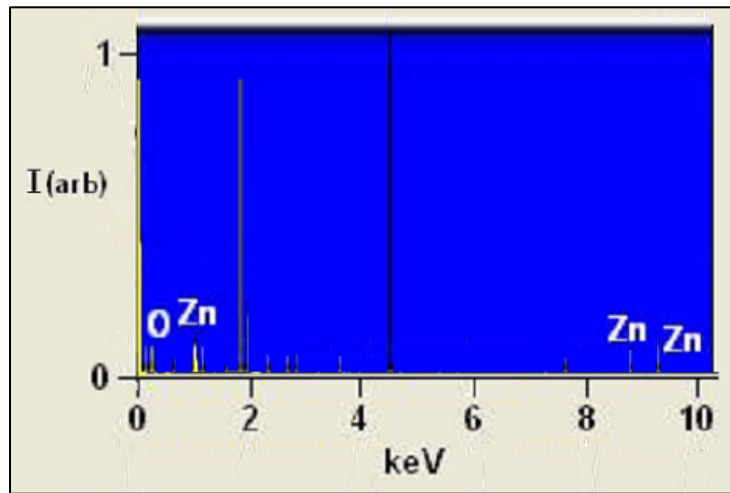

Figure 4. EDX spectrum for RT PLD of ZnO on mylar.

The spectra for both the ZnO/mylar and ZnO/paper showed peaks associated with Zn and O. Whilst the O peak could be from the substrate and/or microscope ambient, the Zn peak only appeared after the ZnO deposition. Thus it was concluded that a film had been formed by PLD. Four point electrical measurements before and after deposition confirmed this. Prior to deposition, both substrates showed infinitely high resistance. After deposition, the ZnO on mylar had a resistance of $575 \pm 20\ \Omega$ and the ZnO on paper had a resistance of $30\ 000 \pm 20\ 000\ \Omega$. Assuming that the deposition had formed continuous layers on the paper and mylar (rather than impregnating them) [23], film

thickness was estimated from the deposition times to be about 950 nm. Thus the resistivities were estimated to be approximately 0.25 ± 0.01 Ω.cm for the ZnO on mylar and 13 ± 9 Ω.cm for the ZnO on paper. These are relatively low values.

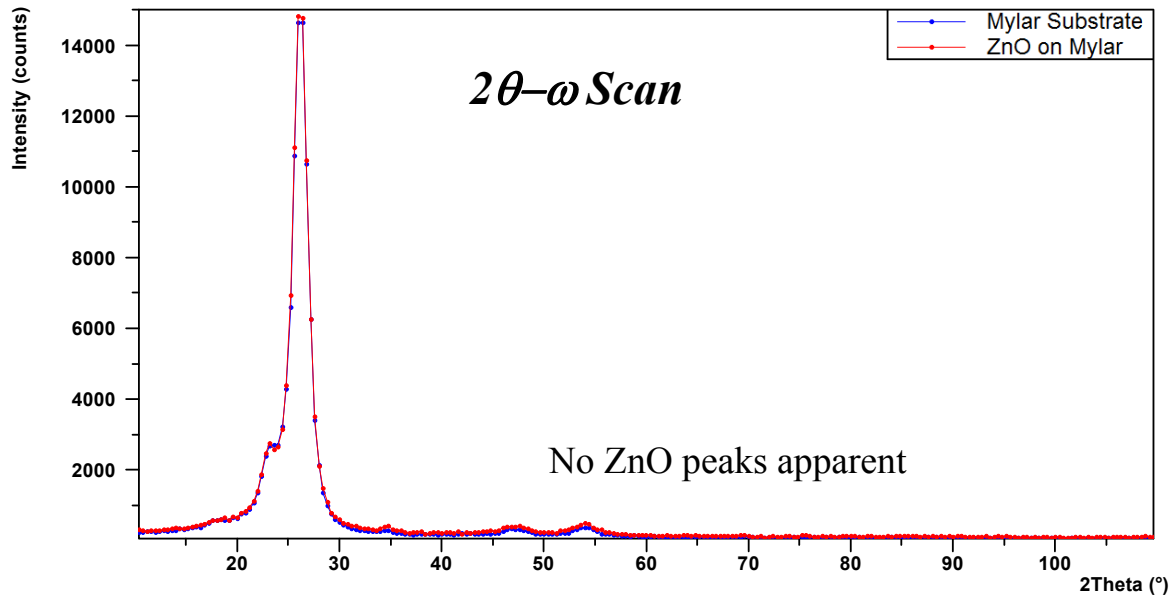Figure 5 shows XRD $2\theta/\omega$ scans for mylar and ZnO/mylar.

Figure 5. XRD $2\theta/\omega$ scans for the mylar substrate before and after RT PLD of ZnO.

The XRD scans were similar before and after ZnO deposition and no peaks associated with crystalline ZnO or Zn were apparent. Figure 6 shows XRD $2\theta/\omega$ scans for paper and ZnO/paper.
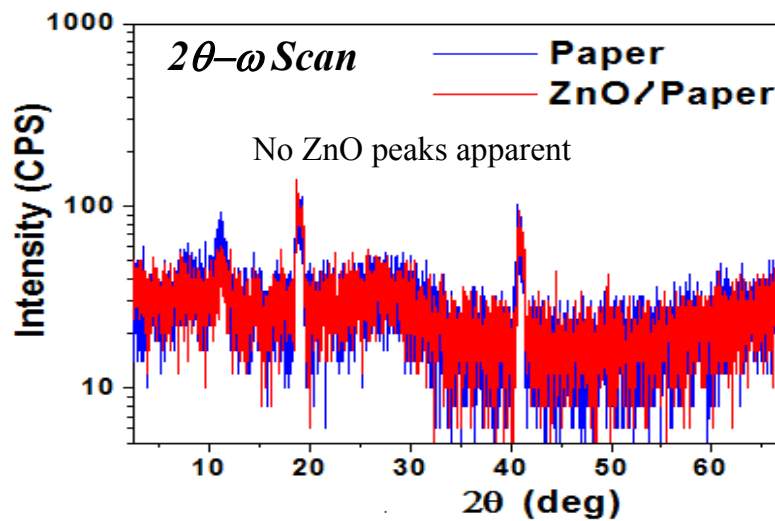

Figure 6. XRD $2\theta/\omega$ scans for a paper substrate before and after RT PLD of ZnO.

Once again, the scans were similar before and after the ZnO deposition and no peaks associated with crystalline ZnO or Zn could be found.

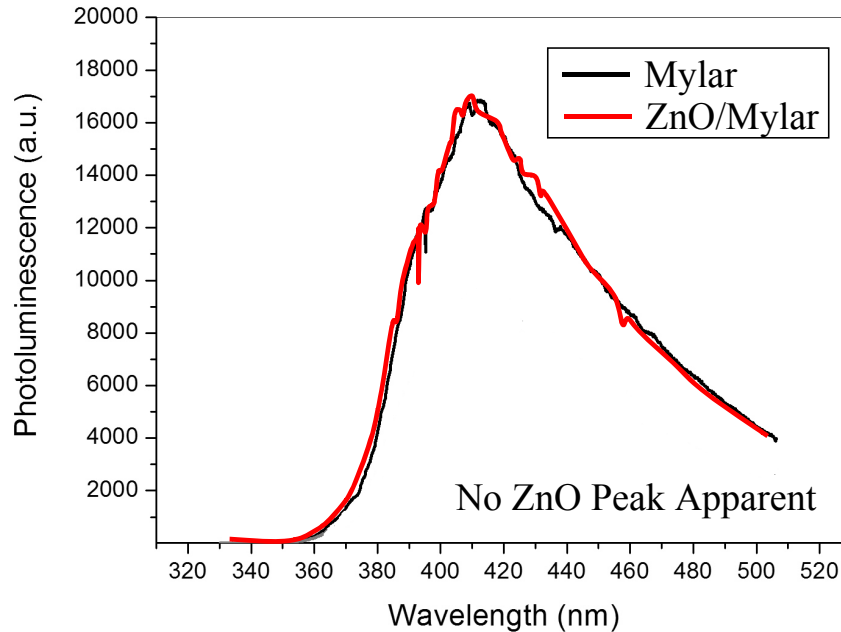Figure 7 shows the PL spectra for mylar and ZnO/mylar.

Figure 7. RT PL spectra for mylar before and after RT PLD of ZnO.

No peaks associated with the ZnO deposition could be found. PL studies for both the paper and the RT PLD ZnO on paper gave no significant signal.

4. CONCLUSION

ZnO thin films were made by PLD onto mylar and paper substrates held at RT. SEM and EDX studies indicated that a ZnO coating had been applied without destroying the integrity of the substrates. 4 point resistance measurements confirmed the presence of conductive layers having relatively low resistivities. XRD studies showed no supplementary peaks after ZnO deposition, and none which could be indexed to crystalline ZnO or Zn. UV RT PL studies showed no supplementary peaks after ZnO deposition and no response characteristic of wurtzite ZnO. Thus, there was no sign of crystallinity. Since the nature of PLD allows for significant flexibility in the adatom mobility and oxidant partial pressure, it is suggested, that RT PLD could be used to engineer ZnO-based AOS layers with enhanced electrical and optical properties directly at RT. It may thus be possible to avoid the inconvenient post-deposition annealing step that is generally required using other deposition techniques.

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