Invited Paper

ZnMgO-based UV photodiodes: a comparison of films grown by spray pyrolysis and MBE

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ABSTRACT

Detecting the UV part of the spectrum is fundamental for a wide range of applications where ZnMgO has the potential to play a central role. The shortest achievable wavelength is a function of the Mg content in the films, which in turn is dependent on the growth technique. Moreover, increasing Mg contents lead to an electrical compensation of the films, which directly affects the responsivity of the photodetectors. In addition, the metal-semiconductor interface and the presence of grain boundaries have a direct impact on the responsivity through different gain mechanisms. In this work, we review the development of ZnMgO UV Schottky photodiodes using molecular beam epitaxy and spray pyrolysis, and we analyze and compare the physical mechanisms underlying the photodetector behavior.

Keywords: ZnO, ZnMgO, photodetector, UV, MBE, spray pyrolysis

1. INTRODUCTION

ZnO has a bandgap that lies in the near UV and thus can play a leading role in light photodetection in this spectral region. Indeed, UV photodetection includes a wide range of applications, which may be grouped in two areas: UV astrophysics and astronomy, and UV terrestrial applications. The first group includes several applications such as solar and astronomical UV imaging, and secure space-to-space communications (both inter- and intra-satellite). The second group includes monitoring of sun UV light exposure of the population, biological and chemical sensors (ozone, pollution in air, biological agents, etc.) and fire/flame detection (fire alarm systems, combustion engine control, missile plume detection).

To cover both the near UV (down to 300 nm) and mid UV (down to 200 nm, including the solar blind region), the ternary ZnMgO needs to be used. By adding Mg to ZnO, the bandgap can be potentially tuned from 3.37 up to 6.2 eV with a wurtzite structure. However, as it was already shown in the early 2000's with different growth techniques (MBE [1], PLD [2] and MOCVD [3]), increasing the Mg content eventually produces a phase separation, and the cubic structure appears, where MgO is stable. It is this maximum Mg content before phase separation that determines the minimum achievable cutoff wavelength. Moreover, the appearance of phase separation, as well as the presence of crystal defects, directly limit the performance of the ZnMgO UV photodiodes (PD). We compare here PDs realized on material grown by two very different techniques: molecular beam epitaxy (MBE) and spray pyrolysis (SP), where the maximum achievable Mg is quite different, and where the physical mechanisms limiting the responsivity are also quite different.

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2. EXPERIMENTAL DETAILS

The ZnMgO structures grown by MBE were deposited on r-plane sapphire (Fig. 1). The MBE-grown ZnMgO structures were 1 μm-thick, with a a-plane orientation. Details of the growth can be found in [4]. The stoichiometry, substitutional character of Mg, and crystallinity was assessed by a combination of Rutherford Backscattering Spectroscopy (RBS), channeling RBS, and XRD [5]. The Mg content shown in Table 1 was extracted from these measurements, and the Mg substitutional character was confirmed for almost all Mg contents, whereas no cubic intrusions where observed. Thus, the single wurtzite crystal character was confirmed up to 56% Mg. Moreover, the RBS channeling analysis shows a yield that is comparable to that from state of the art ZnO substrates, indicative of the high crystal quality of the films.

The SP films were deposited on a-sapphire with a 200-500 nm thick, and a c-plane orientation Details on the growth can be found in [6]. The Mg content in these films could not be properly quantified by RBS due to the fact that they show some porosity. Thus, EDX spectroscopy was used instead, yielding the values shown in Table 1.

The metal layers were deposited by e-beam evaporation under high vacuum conditions. In the MBE-grown material, semitransparent Au-Schottky photodiodes 100 Å-thick using circular structures of diameter 200 μm were fabricated coplanar to the ohmic contacts, which consisted of an annealed 1000 Å-thick Ti/Al/Ti/Au layer. The samples were exposed to a H_2O_2 pre-treatment to passivate the surface, which has been previously shown to lead to very high quality Schottky contacts on (Zn,Mg)O/ZnO PDs [7]. In the SP-grown material, metal-semiconductor-metal (MSM) contacts were realized with 800 Å-thick Au layers [8]. In this case, no H_2O_2 pre-treatment was used because of the high porosity of the films. For the responsivity analysis, a 1000 W-Xe lamp with a 1/4 m monochromator were used to excite the photodiodes.

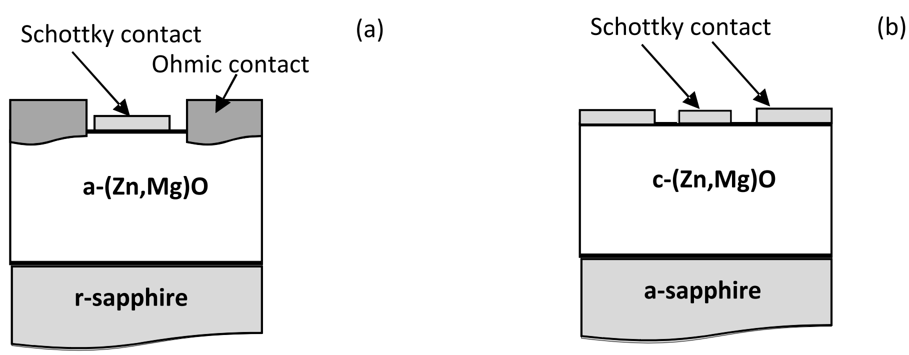

Figure 1. Schematic of the Schottky (a) and MSM (b) photodiodes on the MBE and SP layers, respectively.

Table 1. Details of the photodiodes, their growth technique and the measured Mg content.

Growth technique	Sample	% Mg
Molecular Beam Epitaxy	MBE1	0
	MBE2	31
	MBE3	44
	MBE4	52
	MBE5	56
Spray Pyrolysis	SP1	0
	SP2	6
	SP3	8
	SP4	14
	SP5	22
	SP6	30
	SP7	35

3. RESULTS AND DISCUSSION

3.1 MBE-grown Schottky UV photodiodes

A detailed analysis of the IV curves from the photodiodes under dark conditions shows that the diodes have ideality factors between 1.2 and 1.8, Schottky barriers above 1.0 eV and low reverse saturation currents in the 10^{-8}-10^{-11} A/cm^2 range. In addition, the rectification ratio between forward and reverse biases is as high as 10^7-10^9 [9].

Table 2. Details of the PD figures of merit, including Schottky barrier (Φ_b), ideality factor (n), series resistance (R_s), reverse saturation current (J(-2V)), and current rectification ratio (J(+2V)/J(-2V)).

Photodiode	Φ_b(eV)	n	R_S(Ωcm^2)	J(-2V) (A/cm^2)	J(+2V)/J(-2V)
MBE1	1.2	1.2	1.78	$-2x10^{-9}$	$\sim 10^8$
MBE2	1.2	1.4	5.52	$-1x10^{-8}$	$\sim 10^8$
MBE3	1.2	1.6	16.00	$-1x10^{-11}$	$\sim 10^9$
MBE4	1.0	1.7	16.36	$-6x10^{-11}$	$\sim 10^8$
MBE5	1.0	1.8	11.71	$-3x10^{-10}$	$\sim 10^7$

The spectral response of the photodiodes was analyzed and the cutoff energy of the detector determined. As shown in Fig. 2 the cutoff energy can be tuned from 3.3 eV for the ZnO photodiode, up to 4.7 eV (264 nm) by increasing the Mg content up to 56 %. These short wavelengths already are in the solar blind region of the spectrum. The high quality of the Schottky photodiodes is evident from the very large UV/VIS spectral rejection ratios that are in the 10^4-10^6 range. Indeed, detail analysis of the crystal structure of these films [5] shows that there are no cubic intrusions up to 56% Mg, the Mg sits in a substitutional site even in the high Mg content films, and the RBS channel yield is close to the state of the art commercial single crystal ZnO substrates. Thus, the high crystal quality allows reaching the solar blind region while keeping the wurtzite structure. This high crystal quality is also responsible for the quite reasonable responsivities, which in the 56 %Mg photodiode is around 0.1 A/W (i.e., with internal quantum efficiency below 100 %), with no indication of any internal gain.

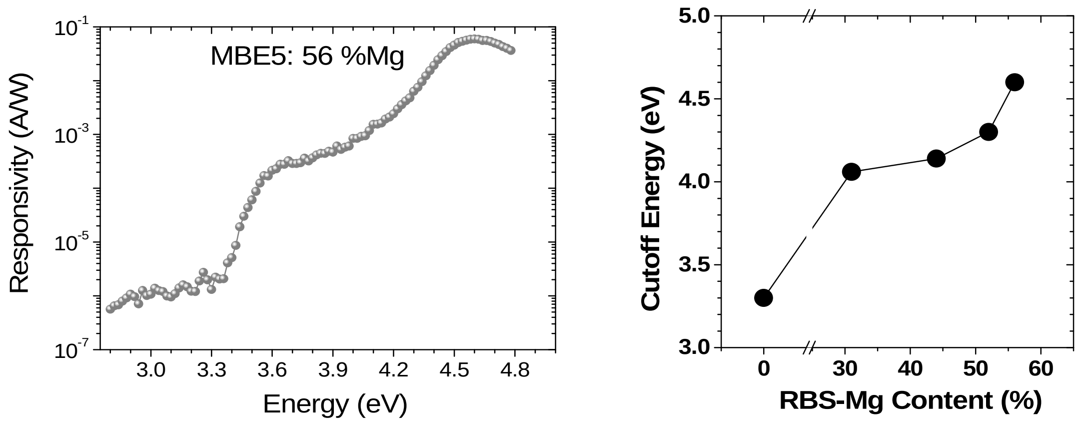

Figure 2. Left: Spectral response at -1.5 V from the Schottky Photodiode with the highest Mg content. The feature at 3.4 eV is the absorption from the ZnO buffer layer. Right: Cutoff energy of the Schottky photodiodes as a function of the Mg content in the film.

3.2 SP-grown MSM UV photodiodes

The SP-based MSM photodetectors show quite dark currents (Fig. 3), shifting from 10^{-3} A at -4 V in the reference ZnO MSM, down to 10^{-9} A also at -4 V, in the 35% Mg photodiode. This decrease in dark current with increasing Mg content is likely related to two factors. First, increasing the Mg content typically yields a lower carrier concentration in the ZnMgO film, producing more resistive layers [10]. Second, and most important in this case, the grain size decreases with increasing Mg content, yielding larger grain boundaries respect to the volume of the crystal [8]. This effect also directly affects the total carrier concentration and mobility of the films, such that films with small grains show much larger resistivities due to carrier trapping/scattering at the boundaries.

However, during illumination the photocurrent increases quite dramatically, yielding photocurrents in the 10^{-2}-10^{-3} A range, i.e., many orders of magnitude larger than the dark current for the high Mg MSM photodiodes. This illuminating/dark current ratios are thus in the 10^1 range for ZnO and as high as 10^7 for the high Mg MSM photodiode (see inset of Fig. 3). This is the result of above mentioned effect on the dark current, as well as the very high responsivities in these films, which are in the 10^2-10^3 A/W range. These responsivities yield internal quantum efficiencies well above 100%, indicating a strong internal gain. This gain can be explained to arise from photo-generated carriers that are trapped at the grain boundaries, producing a strong photoconductive gain.

These MSM photodiodes made with SP films allows yielding cutoff energies up to 4.02 eV (309 nm), but with very limited UV/VIS rejection ratios of only 10^1-10^2. The large absorption tail observed below bandgap correlates quite well with the very large Stokes shift in these films, which increases with the Mg content up to 275 meV for 35 % Mg [8]. However, as it was mentioned above, the extremely large illumination/dark current ratios above bandgap can be quite attractive for applications that require very high sensitivity but limited selectivity and response time, for a fraction of the price that is required to make an MBE-based UV photodiode.

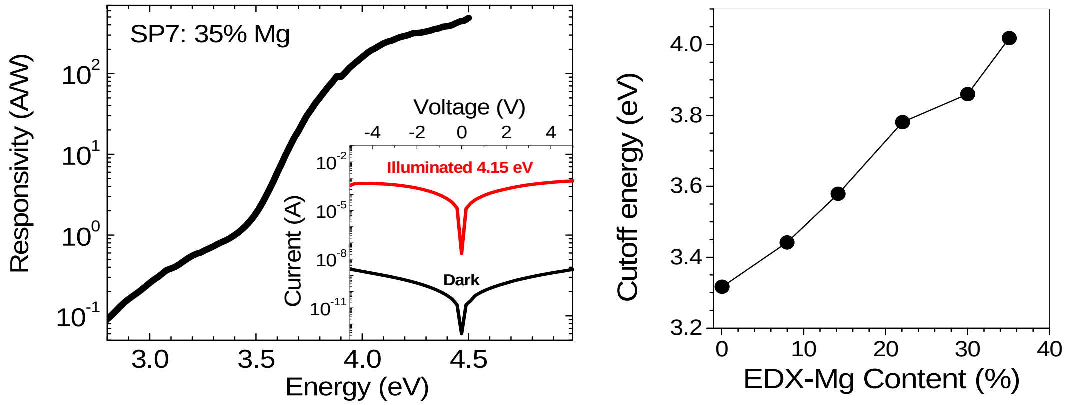

Figure 3. Left: Responsivity of SP-MSM photodiode at 4V with the highest Mg content. Right: Cutoff energy of the SP-MSM photodiodes as a function of the Mg content in the film.

4. CONCLUSIONS

We have shown that both MBE and SP photodiodes can be used to cover part of the UV spectrum. With MBE ZnMgO films, the Mg concentration can be increased up to 56 % without phase separation and high crystal quality, yielding absorption cutoff energies up to 4.7 eV (264 nm), in the solar blind region. These Schottky photodiodes have UV/VIS rejection ratios of up to 10^6, with responsivities in the 0.1 A/W for the highest Mg content, and no indication of internal gain. In contrast, SP allows incorporating Mg contents up to 35 % before phase separation, yielding absorption cutoff energies around 4 eV (309 nm) for MSM photodiodes. The SP films are however polycrystalline, with grain sizes decreasing with the Mg content. This has a direct effect on the presence of a large internal photoconductive gain, which yields responsivities in the 10^2-10^3 A/W. However, because of the very low dark current associated with the charge trapping/scattering at the grain boundaries, which happens in parallel to the large responsivities due to the photoconductive gain, produces illumination/dark current ratios as high as 10^7, which is quite attractive for specific applications where a high sensitivity and low selectivity is needed.

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