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Full Length Article

Morphology, stoichiometry, and crystal structure control via post-annealing for Pt–ZnO nanograin Schottky barrier interfaces

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ABSTRACT

Nanointerfaces have attracted intensive research effort for advanced electronics due to their unique and tunable semiconducting properties made possible by metal-contacted oxide structures at the nanoscale. Although much work has been on the adjustment of fabrication parameters to achieve high-quality interfaces, little work has experimentally obtained the various correlations between material parameters and Schottky barrier electronic properties to accurately probe the underlying phenomenon. In this work, we investigate the control of Pt–ZnO nanograin interfaces properties by thermal annealing. Specifically, we quantitatively analyze the correlation between material parameters (such as surface morphology, crystallographic structure, and stoichiometry) and Schottky diode parameters (Schottky barrier height, ideality factor, and contact resistance). Results revealed strong dependencies of Schottky barrier characteristics on oxygen vacancies, surface roughness, grain density, *d*-spacing, and crystallite size. *I-V-T* data shows that annealing at 600 °C produces a nanograin based interface with the most rectifying diode characteristics. These dependencies, which have not been previously reported holistically, highlight the close relationship between material properties and Schottky barrier characteristics, and are instrumental for the performance optimization of nanostructured metal-semiconductor interfaces in advanced electronic devices.

1. Introduction

As the demand for advanced nanoelectronic devices continues to rise, significant research has been directed toward semiconductor nanostructures and nanointerfaces. Nanostructures form a new class of materials that exhibit unprecedented electrical, optical, and mechanical properties [1]. The emergence of transitional metal oxides in nanostructured forms has provided novel morphologies with large surface areas and tunable defect characteristics, which in turn give rise to new transport phenomena and unique electronic properties [2,3].

Oxides and metals can be exploited to form metal-semiconductor interfaces, which are fundamental building blocks of all electronics at both the micro and nano scales. These interfaces are also known as Schottky contacts, with wide device applications from energy harvesting [4], photo detection [5], signal rectification [6], and sensing [7,8]. It is well-known that the quality of Schottky contacts is one of the most critical factors that determine the performance of field-effect transistors and other advanced semiconductor devices [9]. For a Schottky contact formed on an *n*-type oxide surface, the workfunction of the metal is significantly greater than the electron affinity of the semiconductor. For an ohmic contact, the metal workfunction is close to or less than the electron affinity.

Fundamental to the advancement of the field of Schottky interfaces is the scaling of electrical contacts to small dimensions. Departing from the conventional flat and uniform morphology of bulk devices, nanostructured contacts exhibit abruptly angled surfaces, leading to new defect structures and electric field distributions [3]. Therefore, the control of electrical properties of the contact becomes of importance and is ultimately critical to overall device performance. Carrier transport across Schottky interfaces are typically governed by band offset or the Schottky barrier height (SBH) [10]. The ability to systematically tune the Schottky barrier height represents one of the biggest challenges to the nanoscale research community. It has already been reported that nanostructured contacts behave differently than their macroscopic, bulk counterparts [11]. The formation of Schottky interface using nanostructured oxides is established under the influence of surface defects, which in excess, can lead to significant degradation in rectifying characteristics, as indicated by the ideality factor deviating from unity.

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To form high-quality Schottky contacts, various metal oxides such as TiO_2, SnO_2, and ZnO have been investigated [12,13]. ZnO has attracted intense research efforts owing to its unique photocatalytic [14] and electrical [15] properties. Studies have also provided qualitative discussions of the relationship between fabrication conditions and the resultant electronic properties of nanostructured ZnO [16,17]. Post-fabrication processes such as thermal annealing have also been shown to affect electronic properties at the interface [8,18,19]. Sheu et al. has investigated thermal annealing on electrical resistivity of sputtered Ga-doped ZnO [20]. Sekhar et al. has reported resistive switching features on rapid thermal annealed ZnO film prepared by PLD [21]. Lee et al. has studied the effect of rapid thermal annealing on the rectifying behavior of ZnO/NiO heterojunction [22]. Although much work has been done, the connection between the materials properties (e.g. morphology, crystallographic structure, and stoichiometry) and their resulting electronic properties (e.g. rectifying behavior) of nanostructured Schottky interfaces have yet to be optimized and fully understood.

In this paper, we report the dependency of Schottky characteristics on a wide array of material properties at the nanostructured Pt–ZnO interfaces and explain the phenomenon governing such dependencies. We quantitatively analyze the dependencies of electronic properties on barrier formation by optimizing the annealing temperature. From current-voltage-temperature (*I-V-T*), Schottky interface parameters (barrier height ϕ_b, ideality factor η, and series resistance R_S) are analyzed alongside with material characteristics, including surface morphology (roughness and grain density), crystallographic structure (*d*-spacing and crystallite size), and stoichiometric composition (oxygen vacancies). The correlations between the material and electronic properties of nanostructured Schottky barriers are analyzed and discussed.

2. Experimental

In this work, six ZnO nanograin films were prepared by pulse laser deposition (PLD), which had previously been shown to create highly crystalline nanograin films [23]. The deposition chamber was vented via a cryogenic pump down to a base pressure of 5×10^{-4} mbar. Prior to deposition, substrates were heated to 200 °C, and pure O_2 gas was allowed to flow into the chamber at a working pressure of 0.133 mbar. During deposition, a KrF (248 nm) excimer laser was maintained at an output power of 300 J, pulsed at 5 Hz. The laser beam was focused onto a rotating 99.99%-pure ZnO target, with *n*-type Si (0 0 1) substrates positioned at a distance 50 mm away. Deposition was conducted for 20 min, which grew nanostructured ZnO film with a thickness of approximately 20 nm, measured by a calibrated quartz thickness monitor. In order to establish a method of forming high-quality Schottky barriers, a range of post-annealing temperatures were investigated. The as-grown ZnO samples underwent thermal post-annealing in Ar gas for temperatures from 400 to 800 °C in 100 °C intervals. After post-annealing, the Schottky (Pt) and ohmic (Ti/Pt) contacts were sequentially deposited through a stainless steel shadow mask. Prior to deposition, ZnO samples were heated to 200 °C. A sputtering power was set to 100 W. The average thickness of the metal contacts was calibrated by a quartz crystal microbalance. 99.99% (Sigma Aldrich) pure Ti and Pt sputtering targets were used. The base pressure of the chamber was 6.7×10^{-5} mbar and the working pressure using pure Ar gas was maintained at 6.7×10^{-3} mbar. The ZnO samples were heated inside the sputtering chamber at 200 °C during deposition to form the ohmic and Schottky contacts. Pt was selected as it has a high work function transition metal with good thermal stability [24]. During electrical characterization, connections to the device are provided by two Au microprobes contacting the electrodes. *I-V-T* characteristics were measured by using a Keithley 2400 source meter.

3. Results and discussion

3.1. Surface morphology

Fig. 1(a) shows an SEM surface scan of the as-grown ZnO nanograin morphology revealing the nanocrystallites and nanograins. Fig. 1(b) shows a cross-sectional SEM at 45° to the surface of the ZnO nanograins. The trench is etched by SEM focused Ar ion beam revealing an underlying film thickness of 20 nm. Fig. 2 shows an AFM surface scan of a 1×1 μm section from the as grown ZnO nanograin film showing the surface of the nanograins. Fig. 2(a) depicts the as-grown film, and Fig. 2(b)–(f) shows nanograins annealed at 400, 500, 600, 700, and 800 °C, respectively. Results indicate that the nanograin size increases with respect to annealing temperature. The formation of larger nanograins can be explained by the Ostwald ripening effect [25], which suggests that as ZnO film is heated, thermal energy facilitates the coalescence of nanostructured nanograins. Coalescence can be explained by the fact that Zn and O atoms gain thermal energy during the annealing process, thus are able to diffuse throughout the film and promote growth where the nanograins can coalesce together to form a larger granular cluster. Such coalescence can also promote the formation of larger homogenous crystals throughout the film. This is consistent with previous observations on ZnO film growth [26,27].

Fig. 3 plots the root-mean-square (RMS) surface roughness and grain density as measured by AFM across annealing temperatures. The RMS surface roughness increases with annealing temperature as grains becomes larger at high annealing temperatures. Between annealing temperature of 500–800 °C, RMS surface roughness increases from 22.6 to 60.4 nm. These results show that, as larger nanograins are formed the RMS surface roughness increases A similar trend has been reported previously [28,29]. This is also confirmed by the decreasing grain density (plotted on Fig. 3(a), right axis) as the annealing temperature increasing. Formation of larger grain sizes can also be attributed to the lowering of the surface energy during growth.[30] The grain diameter increases from 21.4 nm to 74 nm (determined from AFM analysis software Gwyddion) when the annealing temperature increases from 400 to 800 °C. This behavior is consistent with similar nanomaterials. [27,31] As the grain size increases due to merging of neighbouring grains, the overall surface area decreases. However, as greater grain density is achieved, the surface area increases, which results in two opposing trends. With these two trends plotted in Fig. 3(a), the correlation between them converges at an annealing temperature of 600 °C, which signifies the post-annealing condition with the highest grain density and lowest roughness is achieved.

Fig. 3(b) shows the distribution of the nanograin heights for the samples annealed at different temperatures. The distribution can be seen as Gaussian, with the nanograins annealed at 800 °C showing the broadest distribution and the highest nanograin height. Nanograins annealed between 400 and 700 °C appear to provide narrower height distributions, which suggest that nanograins coalesce uniformly with respect to increasing annealing temperature. The FWHM of the peaks is narrow for sample annealed at 600 °C, at which the nanograin sizes with the highest median height and narrowest distribution are observed.

3.2. Crystal structure

Fig. 4(a) depicts the XRD diffractogram of as-grown and annealed ZnO nanograin films using a Cu Kα source (0.154 nm). A dominant peak at 34.4° (2θ), corresponds to a single crystal