

Thermal Conductivity of Bulk ZnO after Different Thermal Treatments

[Journal of Electronic Materials](#), [Apr 2006](#) by [Özgür, Ü](#), [Gu, X](#), [Chevtchenko, S](#), [Spradlin, J](#), [Et al](#)

Thermal conductivities (κ) of melt-grown bulk ZnO samples thermally treated under different conditions were measured using scanning thermal microscopy. Samples annealed in air at 1050°C for 3 h and treated with N-plasma at 750°C for 1 min. exhibited $\kappa = 1.35 \pm 0.08$ W/cm-K and $\kappa = 1.47 \pm 0.08$ W/cm-K, respectively. These are the highest values reported for ZnO. Atomic force microscopy (AFM) and conductive-AFM measurements revealed that surface carrier concentration as well as surface morphology affected the thermal conductivity.

Key words: ZnO, thermal conductivity, atomic force microscopy (AFM), conductive AFM

INTRODUCTION

The semiconductor ZnO has lately gained substantial interest in the research community, fueled and fanned by its prospects in optoelectronics applications owing to its direct wide bandgap ($E^{\text{sub}}_g \sim 3.3$ eV at 300 K) and large exciton binding energy (60 meV).¹ Some optoelectronic applications of ZnO overlap with that of GaN, another wide bandgap semiconductor ($E^{\text{sub}}_g \sim 3.4$ eV at 300 K) that is widely used for production of green, blue-ultraviolet, and white light emitting devices.² However, ZnO has some advantages over GaN, among which are the availability of fairly high-quality ZnO bulk single crystals and a much simpler crystal growth technology, resulting in a potentially lower cost for ZnO-based devices. ZnO is also considered as a promising candidate for GaN epitaxy mainly due to the fact that the lattice mismatch between GaN and ZnO is very small compared to that with the most commonly used substrate, sapphire. Despite having a relatively small lattice mismatch with GaN, SiC is a very expensive substrate to produce, and due in part to its different stacking order from that of GaN, structural defects such as inversion domain boundaries and stacking mismatch boundaries become inevitable. Using the wurtzite structure, ZnO as a substrate is expected to avoid such structural defects. Besides the crystal structure, the thermal mismatch between the GaN and ZnO is also relatively small, which is about half of that between GaN and SiC. Due to the lack of large area and affordable GaN bulk substrates, ZnO remains the only isomorphic substrate for GaN epitaxy. Device design also

can be relatively simple because ZnO substrates are usually conductive, allowing vertical electrical injection in potential vertical devices. Most of the applications for the above-mentioned wide bandgap materials are related to high power electronic and optoelectronic devices; therefore, it is essential to understand the thermal characteristics. It has been shown that using different surface treatments, smooth ZnO surfaces can be prepared for GaN epitaxy.

To date, there have been very limited studies of thermal conductivity (κ) in ZnO.^{3–7} Most of the works were mainly on powder ZnO, which reported very low thermal conductivities at room temperature.^{3–6} Later on, availability of better quality bulk ZnO samples led to larger values for thermal conductivity mostly due to improved sample quality.⁷ Here, we report on the effects of different thermal treatments on the thermal conductivity κ of several bulk ZnO (0,001) samples grown by Cermet, Inc.⁸ using the melt growth technique.

EXPERIMENTAL PROCEDURE

RESULTS AND DISCUSSION

Figure 1 shows the $5\ \mu\text{m} \times 5\ \mu\text{m}$ area AFM scans for the four samples investigated. The root-meansquare (rms) surface roughness values obtained from these scans were 4.4 nm, 2.2 nm, 0.5 nm, and 2.3 nm for the as-received, FG-annealed, airannealed, and N-plasma-treated samples, respectively. These results clearly indicate that after all kinds of treatments used here, the Zn-face bulk ZnO samples still have smoother surfaces compared to that of the as-received O-face ZnO. Here, we should also indicate that the Zn face as-received ZnO samples had very smooth surfaces with no indication of atomic features (rms roughness: 0.2 nm).

Results from thermal conductivity measurements performed at different points on each sample using SThM are listed in Table I. Two random areas well separated from each other were chosen on samples of $5\ \text{mm} \times 5\ \text{mm}$ size. The variations represent standard deviations in κ determined by multiple measurements in these random areas. The κ values for the as-received sample, $\kappa = 1.00 \pm 0.08$ and $0.95 \pm 0.06\ \text{W/cm-K}$, are consistent with the previously reported values for the untreated bulk ZnO samples ($\kappa = 1.16 \pm 0.08\ \text{W/cm-K}$ and $1.02 \pm 0.07\ \text{W/cm-K}$ and $\kappa = 1.10 \pm 0.09\ \text{W/cm-K}$ and $0.98 \pm 0.08\ \text{W/cm-K}$ for the Zn-face and O-face ZnO, respectively).⁷ On the FG-annealed sample at both positions, κ is considerably smaller ($\kappa = 0.67 \pm 0.08\ \text{W/cm-K}$ and $0.46 \pm 0.05\ \text{W/cm-K}$). To be consistent with the earlier models, this would indicate that forming gas annealing has resulted in increased surface roughness, which has considerably reduced κ due to the decrease in $L(T)$ in Eq. 1. The AFM scan in Fig. 1b shows that the surface in fact is somewhat rough; however, the rms roughness is smaller than that for the as-received sample

that exhibited higher κ . Therefore, the reduction in κ cannot be explained only by increased surface roughness. For the air-annealed and N-plasma-treated samples, the measured values for κ are higher and the values for the N-plasma-treated sample ($\kappa = 1.44 \pm 0.08$ W/cm-K and 1.47 ± 0.08 W/cm-K) are the highest κ values reported so far for ZnO. One may argue that air annealing and nitrogen plasma treatment both have resulted in a good surface compared to the as-received sample. This is true especially for the air-annealed sample, as seen in Fig. 1c, where atomic steplike features are clearly visible. However, the surface morphology of the N-plasma-treated samples is similar to that of the FG-annealed sample, and its surface roughness (2.3 nm rms) is larger than that of the air-annealed sample (0.5 nm rms).

For a better understanding of these results, it is constructive to refer to the reports on thermal conductivity of GaN. For partially coalesced epitaxial lateral overgrown GaN/sapphire (0001) samples, a correlation between low threading dislocation density and high thermal conductivity values was established. The reduction in the thermal conductivity with increased dislocation density is expected as threading dislocations degrade the sound velocity and increase the phonon scattering in the material. Calculations by Kotchetkov et al.¹³ show that κ remains fairly independent of extended defect concentration ($D^{\text{sub}} d^{\text{^}}$) up to some characteristic value $D^{\text{sup}} \text{char}^{\text{^}} d^{\text{^}}$ after which it decreases about a factor of 2 for every decade increase in $D^{\text{sub}} d^{\text{^}}$. The thermal conductivity has also been correlated to doping levels in hydride vapor phase epitaxy n-GaN/sapphire (0001) using SThM on two sets of samples.¹⁴ In both sets of data, the thermal conductivity decreased linearly with $\log n$, n being the electron concentration in Eq. 2, the variation being about a factor of 2 decrease in κ for every decade increase in n . Significantly, it was concluded that the decrease in the lattice contribution to κ (Eq. 1), due to increased phonon scattering from impurities and free electrons, outweighs the increase in the electronic contribution to κ (Eq. 2). Similarly, for ZnO, using Eq. 2 with $n = 10^{\text{sup}} 19^{\text{^}} \text{cm}^{\text{sup}} -3^{\text{^}}$ and $\tau \sim 10^{\text{sup}} -14^{\text{^}} \text{s}$ (assuming an electron mobility of $100 \text{cm}^{\text{sup}} 2^{\text{^}}/\text{V-s}$), one can calculate an electronic contribution of $\kappa^{\text{sub}} \text{electr}^{\text{^}} \sim 10^{\text{sup}} -3^{\text{^}} \text{W/cm-K}$, which is negligible when we consider the values measured here. Therefore, by increasing/decreasing electron concentration, one may expect a more pronounced decrease/ increase in the lattice contribution to the thermal conductivity in ZnO.

The variation in κ observed here for bulk ZnO samples may partially be due to the increased/ decreased number of surface defects caused by the post treatment. However, the increased optical quality for the FG-annealed sample, which suggests reduction of surface defects, does not correlate with the observations of decreasing thermal conductivity. As a kind of reduction treatment, the thermal treatment in forming gas has been observed to cause significant release of Zn vapor in ZnO powders and has resulted in extra singly

occupied oxygen vacancies ($V^{\text{sub}} O^{\text{^}}$) giving rise to a green luminescence band in the PL spectra.^{15,16} The surface roughening is mostly caused by the hydrogen in forming gas, which effectively removes the damaged layer on the surface of ZnO. This improvement of crystal quality at the surface is confirmed by the optical measurements discussed before. Most probably, the improvement of the optical quality by the removal of this damaged surface layer is larger than the probable degradation of the surface by introduction of point defects ($V^{\text{sub}} O^{\text{^}}$). Therefore, one cannot argue that the increase in the surface defect density is the dominant mechanism in reducing κ .

At the present time, we have no information about the carrier concentrations/doping levels and their distribution for any of the treated samples. The Hall measurements on the as-received bulk ZnO sample revealed a carrier concentration of $\sim 2 \times 10^{17} \text{ cm}^{-3}$ and a mobility of $\sim 150 \text{ cm}^2/\text{Vs}$. No reliable data were obtained from Hall measurements on the treated samples mainly due to the parallel conduction in the underlying thick ZnO layer. We speculate that, as in the case of GaN, change in the surface carrier concentration may be the source of varying thermal conductivity of the ZnO sample after different forms of treatment. Supporting this argument are the conductive-AFM (C-AFM) measurements conducted for forward, reverse, and zero bias conditions.¹⁷ Figure 2 shows the AFM and C-AFM scans for $5 \mu\text{m} \times 5 \mu\text{m}$ regions of the FG-annealed and N-plasma-treated bulk ZnO samples. Hysteresis and memory effects observed for the as-received sample were indicative of point defects, near the surface damage, or surface states. The reduced conduction in the spectra of N-plasma-treated samples (see Fig. 2a) indicates that the densities of point defects and surface states/carriers have been drastically reduced, although there is still evidence of point defect type conduction. However, the reduction of point defects should be minimal since the optical data (both time-resolved and continuous wave) suggest very small improvement in the optical quality after N-plasma treatment. In contrast, as seen in Fig. 2a, FG annealing was observed to make the films more conductive. Most of the current peaks, which appear near the pits in Fig. 2a, are above 10 nA, but to show all the conducting regions, the maximum scale is chosen as 50 pA. For the FG-annealed sample, most of the surface is conducting at 3 V bias, and the current averaged over the entire $5 \mu\text{m} \times 5 \mu\text{m}$ area C-AFM scan in Fig. 2a is much larger ($\sim 800 \text{ pA}$) than that for the N-plasma-treated sample (

SUMMARY

In summary, thermal conductivities (κ) of meltgrown ZnO samples were observed to vary with different surface treatments. The value measured for the sample treated with N-plasma at 750°C for 30 min., $\kappa = 1.47 \pm 0.08 \text{ W/cm-K}$, is the highest reported on ZnO. After annealing in air, the thermal conductivity

is observed to increase significantly due to the improvement of surface. C-AFM measurements suggest that it is mainly the change in the surface carrier concentration, that clarifies the contradictory results obtained just by comparing surface morphologies measured by AFM. Further electrical and optical measurements need to be performed to obtain a better understanding of posttreatment-induced changes in surface properties and related effects on thermal conductivity.

ACKNOWLEDGEMENTS

This work was funded by grants from MDA (monitored by Mr. C.W. Litton), ONR (monitored by Dr. C.E.G. Wood), and AFOSR (monitored by Dr. G.L. Witt). Discussions with Professor A.A. Baski and Mr. C.W. Litton were very useful.

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