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Brief Reports

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Photoinduced thermal-conductivity changes in aluminum nitride

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This study of defects in oxygen-doped aluminum nitride (AlN) shows that the charge state of vacancy-impurity complexes controls the microscopic coupling between these defects and the host lattice, and thus controls the macroscopic thermal conductivity of AlN samples. This picture is supported in an experimental study that optically varies the charge state of these complexes while probing thermal conductivity, where decreases as large as 4% have been observed after exposure to ultraviolet radiation. These results are explained utilizing a simple model for phonon-vacancy scattering as a function of defect charge.

A wide range of experimental and theoretical studies have addressed the issue of vacancy-phonon scattering in insulating materials.[1-4] In these studies, treatment of the vacancy ranges from the zero-mass limit of a substitutional impurity (strongly coupled to the lattice[1]) to a massless entity with all bonds to the lattice severed.[2] The vacancy–acoustic-phonon scattering cross section has been predicted to change by a factor of 9 between these two extremes. In this paper, the wide band gap ($E_g \approx 6.2$ eV at 295 K) insulator aluminum nitride (AlN) is utilized as a vehicle for experimentally probing the microscopic interaction between vacancies and the host lattice *as the strength of this interaction is varied* via optical excitation. It will be shown that, as coupling to the host lattice is decreased, a decrease in macroscopic thermal conductivity is observed due to a significant increase in the (phonon) scattering cross section for the photoexcited centers. This work *directly* illustrates the critical role that lattice-defect coupling (as controlled by defect charge) plays in determining the defect–acoustic-phonon scattering cross section in insulating materials.

The variable oxygen content, polycrystalline AlN samples utilized in this study, whose preparation has been described elsewhere,[3] contain isolated regions of yttrium aluminate phases, which were added to enhance densification.[5] The thermal conductivity was measured at 295 K with a laser flash technique utilizing a pulsed CO_2 laser with a wavelength of 10.8 μm. The details of this measurement are discussed in Ref. 6. As was shown by Slack, phonon scattering in this temperature range for polycrystalline AlN with a grain size on the order of several microns is dominated by the contribution from the grains (as opposed to any effect of grain boundaries).[7] Ultraviolet (UV) irradiation of samples, which was performed *in situ* during the thermal conduction measurement at an incident angle of 90° with respect to the front surface of the sample, was accomplished with a Hg(Ar) lamp at 253.7 nm and with an intensity of approximately 8 mW/cm^2.

In Fig. 1 is shown a plot of thermal conductivity versus time for an AlN sample with a thickness of 0.35 mm and an oxygen content of 0.29 at. % ($x \approx 0.0029$). There are three distinct regions of this measurement. During the first time interval ($0 < t < 21$ min), a baseline thermal conductivity is established by performing a heat diffusion measurement every 30 sec in the dark. At $t = 21$ min, the UV source is activated, while thermal conductivity con-

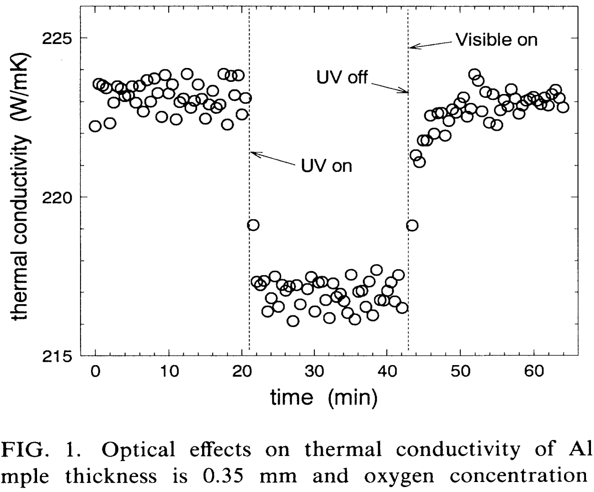

FIG. 1. Optical effects on thermal conductivity of AlN. Sample thickness is 0.35 mm and oxygen concentration is 0.29%.

tinues to be monitored. Note the significant *decrease* in thermal conductivity (about 2.9%) observed after a few minutes of UV exposure. At $t = 43$ min, the UV lamp is extinguished and a visible ($\lambda = 442$ nm) beam illuminates the sample. Visible light at this wavelength has been shown to annihilate centers created by UV exposure.[8,9] Note the rapid *increase* in thermal conductivity that accompanies exposure to this visible light (in the dark, a much slower, temperature-dependent recovery of thermal conductivity is observed). During the course of this measurement, sample temperature was monitored utilizing a thermocouple mounted on the sample. The values in Fig. 1 have been corrected (by $\approx 1\%$) to a uniform temperature to account for the small observed temperature changes ($< 2\,^{\circ}\mathrm{C}$).[10] As is evident from this figure, changes in thermal conductivity significantly above the experimental accuracy of the laser flash technique and *not* attributable to temperature changes are observed when AlN samples are exposed to UV radiation.

In Fig. 2 the data points show the decrease in average thermal conductivity after UV exposure, $\Delta\kappa(L)$, as a function of sample thickness L for samples with $x = 0.0060$ and $x = 0.0029$. Since thermal conduction measurements probe the entire sample thickness, whereas UV irradiation occurs only in a thin layer, this average effect increases significantly as sample thickness is reduced. Note that for a sample with $x = 0.0029$ and $L = 200\ \mu$m, $\Delta\kappa \approx 8$ W/m K is observed.

As is evident from Fig. 2, photoinduced thermal conductivity changes in AlN are related to the oxygen content of the AlN sample. Thus a detailed understanding of the nature of the oxygen-related defect in this material is critical in analyzing the observed changes in thermal conductivity illustrated in Figs. 1 and 2.

Since the work of Slack in 1973, oxygen-related defects in AlN single-crystal and polycrystalline samples have been known to have a controlling effect on thermal conductivity at $T = 295$ K.[1,7] Slack accounted for the change in thermal resistance (W) with oxygen content ($\partial W/\partial x$), by proposing that: (i) oxygen impurities are accommodated substitutionally on the nitrogen sublattice ($\mathrm{O_N}$); (ii) charge is balanced by creating aluminum atom vacancies (V_{Al}) such that $\mathrm{O_N}/V_{\mathrm{Al}} \approx 3$; and (iii) phonon scattering at 295 K is dominated by these vacancies.

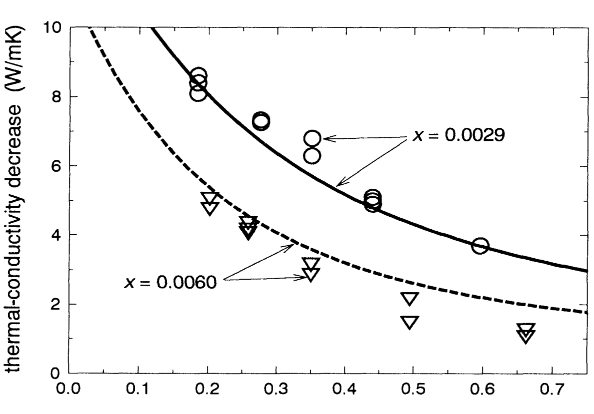

FIG. 2. Thickness dependence of ultraviolet induced thermal conductivity decrease in AlN. Symbols represent data and lines represent a simultaneous one-parameter least-squares fit to Eq. (2) for the two oxygen concentrations indicated in the graph.

In order to calculate $\partial W/\partial x$, Slack utilized an approach proposed by Abeles to account for phonon scattering due to substitutional impurities.[4] In this approach, vacancies are treated as the zero-mass limit of a substitutional impurity using the simple relationship

$$\Gamma = x(1-x)[(\Delta M/M) + \epsilon(\Delta\delta/\delta)]\ , \qquad (1)$$

where Γ is the impurity–acoustic-phonon scattering cross section, $\Delta M/M$ is the mass mismatch between impurity and host lattice, and $\Delta\delta/\delta$ is the size mismatch, which is scaled by an empirically derived parameter ($\epsilon \approx 40$). Slack found good agreement between the calculated value of $\partial W/\partial x$ using this approach and the measured value.

Ratsifaratana and Klemens subsequently used a variational calculation to predict that the perturbation introduced by a vacancy should be some 9 times as large as the Γ predicted by Eq. 1.[2] Physically, Ratsifaratana and Klemens argued that a vacancy is not the zero-mass ($\Delta M = M$) limit of a substitutional impurity, because the vacancy involves severed atomic bonds, which strongly decouple this defect from the host lattice.

A proposed resolution of this discrepancy came when Harris and co-workers presented a model for the evolution of the oxygen-related defect in AlN single-crystal and polycrystalline samples as a function of oxygen content in the AlN lattice.[3,11] As a component of this model, they proposed that the charged nature of the vacancy and its accompanying substitutional oxygen impurity effectively *couples* V_{Al} to the host AlN lattice. The result of this coupling is to decrease the component of vacancy-phonon scattering due to severed bonds, as calculated by Ratsifaratana and Klemens,[3] thereby validating treatment of the vacancy as a massless substitutional impurity (as described by Eq. (1) with $\Delta M = M$). Thus the detailed nature of the coupling of this impurity to the lattice, *as determined by its charge,* significantly effects interaction with phonons and consequently controls thermal conductivity.

In addition to these investigations, optical studies have been performed, which show that oxygen doping leads to UV induced photodarkening of AlN.[8,9] An investigation of this photodarkening effect has recently been conducted by Harris and Youngman utilizing photoinduced absorption spectroscopy.[9] In this study, decreases in the transmission of a visible-light probe ($\lambda = 442$ nm) on the order of 60% were observed after irradiation of the sample with UV light ($\lambda = 252$ nm). This induced absorption effect was probed as a function of oxygen doping levels x, sample thickness L, and probe intensity. The results of these experiments could be understood by proposing the following sequence of light induced transitions. Upon irradiation with UV, an electron (hole) is elevated from the valence band (conduction band) and trapped at the *charged* $\mathrm{O_N}$ *site* (V_{Al} *site*), *thus neutralizing (or partially neutralizing) the impurity-related defect.* When the probe beam is incident on this excited system, the trapped carrier is liberated and elevated to the conduction band (valence band) where radiative recombination can effectively occur. Thus, charged oxygen-impurity-related defects within the AlN lattice (O_N, V_{Al}) result in energy levels within the bandgap, *and the charge state of these defects is changed as they are populated with UV photoexcited carriers, and depopulated via absorption of visible light.*

Utilizing these results, a picture can now be constructed to understand the UV photoinduced changes in thermal conductivity (and visible-light annihilation of these changes) as shown in Figs. 1 and 2. Before UV irradiation, the thermal conductivity of oxygen doped AlN samples is dominated by phonon scattering from aluminum atom vacancies, present as a direct consequence of oxygen substituting for nitrogen in the AlN lattice. Due to the charged nature of these impurity and vacancy sites, V_{Al} is strongly coupled to the host lattice, which significantly decreases the vacancy-phonon scattering cross section. Under these conditions, V_{Al} behaves like the zero-mass limit of a substitutional impurity. Upon UV irradiation, however, these defect sites are populated with carriers with a consequent decrease in charge. Thus, photoinduced population of these defect sites *decreases coupling* to the host lattice and consequently significantly increases the magnitude of the phonon-vacancy scattering cross section. The vacancy in the photoexcited system now behaves according to the predictions of Ratsifaratana and Klemens, whose work indicates a ninefold increase in Γ.[2] Upon exposure to visible light, these defect sites are effectively depopulated, which returns the system to its original charge state, and thus decreases the phonon-vacancy scattering cross section.

In accordance with the discussion above, a model has been constructed to describe the experimental results portrayed in Figs. 1 and 2, which has the following basic tenets: (i) a population of excited centers $n_{ex}(y)$ is created by the UV pump with a spatial distribution $n_{ex}(y) \propto (I_0 \alpha e^{-\alpha y})$ where y is distance into the sample from the UV illuminated surface, α is the absorption coefficient at 253.7 nm, and I_0 is the UV pump intensity; (ii) this excited population may be characterized by a thermal resistivity $W_{ex}(y)$ where $W_{ex}(y) \propto n_{ex}(y)$ so that $\alpha \propto W_{ex}(y=0)$; and (iii) phonon scattering from excited centers occurs in addition to a background of scattering from both unexcited impurity-vacancy centers (characterized by a thermal resistivity W_v) and umklapp processes (W_u). Using this approach, a simple relationship between average thermal resistivity $W(L)$ and sample thickness L may be written:

$$W(L)=W_u+W_v+[W_{ex}(y=0)/(\alpha L)][1-e^{-\alpha L}] . \tag{2}$$

This relationship may now be applied to the measured values of $\Delta\kappa(L)$ versus sample thickness L for different oxygen concentrations shown as symbols in Fig. 2 utilizing: $W_u=(320\ \mathrm{W/m\,K})^{-1}$;[7] the measured dark resistivity results (W_v+W_u) for each sample as shown in the initial portion of Fig. 1; the measured pump absorption coefficients $\alpha(x=0.0029)=65\ \mathrm{cm}^{-1}$ and $\alpha(x=0.0060)=89\ \mathrm{cm}^{-1}$; and the condition that

$$\alpha(x=0.0029)/\alpha(x=0.0060) = W_{ex}(x=0.0029, y=0)/W_{ex}(x=0.0060, y=0) . \tag{3}$$

The lines in Fig. 2 show the best fit of Eq. (2) to both data sets using Eq. (3) and the same single free parameter, $W_{ex}(x=0.0029, y=0)$, which has the value 0.03 cm K/W. The ability to fit simultaneously both data sets of Fig. 2 with Eq. (2) strongly supports the argument that the observed decreases in thermal conductivity with UV irradiation are caused by photoexcitation of oxygen-defect-related centers to a more highly (phonon) scattering state.

A quantitative estimate of the excited defect population can be made by utilizing the derived values of W_{ex} above, the theoretical cross-section difference predicted by Ratsifaratana and Klemens for an unexcited center [$\Delta M=M$ in Eq. (1)] versus an excited center [$\Delta M=3M$ in Eq. (1)],[2] and $W_v=238\ \Gamma$ cm K/W (Ref. 1). At the excited surface, this is found to be on the order of 1.9×10^{18} cm^{-3} and 1.4×10^{18} cm^{-3} for the $x=0.0060$ and $x=0.0029$ samples, respectively.

In this paper, the results of oxygen-related-defect studies on polycrystalline AlN have been utilized to propose that the charge state of impurity-vacancy complexes influences the microscopic coupling between these defects and the host lattice and thus control the macroscopic thermal conductivity of bulk AlN samples. This assertion has been further supported by an experimental study, which varies the charge state of these impurity-defect complexes through the trapping of photogenerated carriers and then probes resulting changes in thermal conduction. In this simple experiment, changes in thermal conductivity as large as 4% ($\Delta\kappa=8$ W/m K) have been observed. When UV excited samples are exposed to visible radiation ($\lambda=442$ nm), which has been shown to liberate charged carriers trapped at impurity-vacancy sites,[8,9] the macroscopic thermal conductivity is observed to return to the original (dark) value, consistent with the mechanism proposed above. Also supporting this picture are the dependences of $\Delta\kappa(L)$ on sample thickness and oxygen concentration, as illustrated in Fig. 2.

This work has demonstrated an important phenomena: that microscopic (optically induced) alterations in a defect's charge state can strongly influence the vacancy-phonon scattering cross section, which is manifested in changes in macroscopic thermal conductivity. This finding provides key insight into the interaction of vacancies and phonons and illustrates an interesting counterpoint to electrical transport measurements, where carrier-lattice interaction alters carrier conduction (i.e., changes in carrier mobility due to polaronic effects). This work also indicates that thermal conductivity measurements may be utilized as an additional probe of the detailed nature of charged defects in insulating materials, with particular sensitivity to changes in the coupling of these defects to the host lattice.

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