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Drop and recovery of thermal conductivity of AlN upon UV irradiation

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Abstract. We have performed calculations of the room-temperature thermal conductivity of oxygen contaminated aluminium nitride (AlN) by employing the Callaway model with a detailed account of three-phonon scattering processes. The role of Al vacancy and O substitution of N has been examined in the form of extended defects (clusters) and point defects. Our work provides support for the theoretical model proposed by Harris et al. [Phys. Rev. B. 47, 5428 (1993)] to explain the experimentally observed drop in the conductivity upon UV irradiation and its recovery upon UV removal and subsequent illumination of the sample with visible light at room temperature. With the reported oxygen concentration in the sample, the scattering of phonons from oxygen-related extended defects is found to be ineffective. Within the picture presented by Harris et al., the point impurity scattering parameter increases by around 17% upon UV irradiation of the sample at room temperature.

1. Introduction
Aluminium nitride (AlN) has been receiving extensive and rapidly growing studies due to its unique properties. Being a material characterised with wide band gap ($E_g = 6.2$ eV at room temperature), high thermal conductivity and low expansion coefficient, AlN is an excellent candidate for optoelectronic and high-temperature applications. The quality of potential optoelectronic and thermal applications of AlN is largely controlled by the quality of its electronic and thermal properties which, in turn, are largely influenced by the nature and number of its native defects and impurities.

Oxygen-related defect complexes are important native defects in several semiconductors. Oxygen is incorporated in AlN via lattice dissolution and appears to be a substitutional impurity [1]. AlN has the ability to accommodate oxygen to levels exceeding 4 at.%. Due to the effect of oxygen on the thermal conductivity of AlN, the mechanism of the large accommodation of oxygen is of high scientific and technological interest [2]. However, the local atomic structure of the oxygen point defects in AlN is still a controversial issue [3]. These defects and impurities scatter phonons, which are the heat carriers in AlN, and thus reduce the thermal conductivity of the material.

Oxygen substitutes for nitrogen in AlN and aluminium vacancies are created as a direct consequence of the compensation of oxygen impurities [1, 3]. In principle, one triply negative Al vacancy is required for three positive donors to satisfy charge neutrality after incorporation of oxygen donors [4]. Theoretical treatment of vacancy-phonon scattering in insulators ranges from the zero-mass limit of a substitutional impurity to a massless entity with all bonds to the lattice severed [5, 6, 7, 8]. In this work, we provide a theoretical support for the simple model suggested...
by Harris et al. [9] through theoretical estimates (based upon more accurate and detailed theory) of the role of oxygen-related defects in AlN in the forms of both point impurities and extended defect complexes (clusters as reported in Ref. [2]).

2. Theory

Within Debye’s isotropic continuum model, Callaway’s expression for thermal conductivity can be written as [10, 11]

\[
K_c = \frac{\hbar^2 q_D^5}{6\pi^2 k_B T^2} \left[ \sum_s c_s^4 \int_0^1 dx x^4 \tau \bar{n}(\bar{n} + 1) + \frac{\left\{ \sum_s c_s^2 \int_0^1 dx x^4 \tau \bar{n}(\bar{n} + 1) \right\}^2}{\sum_s \int_0^1 dx x^4 \tau \bar{n}(\bar{n} + 1)} \right],
\]

where \( c_s \) is phonon speed for polarisation index \( s \), \( q_D \) is the Debye radius, \( x = q/q_D \) is the reduced wave number, \( \bar{n} \) is the Bose-Einstein distribution function.

Oxygen-related defects in AlN occur in two distinct forms: as point defects and as small aggregates (or clusters). Such impurities and defects evolve as a function of oxygen concentration. It is believed that oxygen incorporation generates Al vacancies and oxygen substitution at N sites. For example, it has been proposed that at oxygen concentration below 0.75 at.%, every Al vacancy (\( V_{Al} \)) is surrounded by three substituted oxygen atoms (\( O_N \)), and above 0.75 at.% a \( V_{Al} \) is surrounded by an octahedrally bonded \( O_N \) configuration [2]. Theoretical investigations suggest that oxygen-related defects produce electronic states which lie deep in the band gap of bulk AlN [4, 12]. With this understanding, we express the total phonon relaxation time \( \tau \) as mainly contributed by scattering from boundary, impurities, defects and crystal anharmonicity. For boundary scattering \( \tau_{bs}^{-1} = c/L \), where \( c \) is the phonon speed and \( L \) is the phonon mean free path determined by the crystal size. The point-defect scattering rate is given by [11]

\[
\tau_{md}^{-1} = \frac{\Omega \Gamma}{4\pi \bar{c}^4} \omega^4 = A \omega^4,
\]

where \( \bar{c} \) is the average phonon speed and \( \Gamma = \sum_s f_s \delta M_s \) is the mass-defect scattering parameter. \( f_s \) is the percentage of \( i \)th isotope present in the crystal, \( M \) is the average atomic mass of all the isotopes present in the crystal, \( \delta M_s = |M_s - \bar{M}| \), where \( M_s \) is the mass of \( i \)th isotope. Extended-sized defects, resulting from the \( V_{Al} - O_N \) complex, can scatter small wavelength phonons geometrically and long wavelength like point defects [13].

Following Srivastava’s scheme, three-phonon relaxation time for a phonon with wave vector \( q \) and polarisation \( s \) is expressed as a compound function of frequency and temperature as

\[
\tau_{qs}^{-1}(3 \text{ ph}) = \frac{\hbar q_D^5 \gamma^2}{4\pi \rho \bar{c}^2} \sum_{s' s''} c_s c_{s'} c_{s''} \left[ \int dx' x'^2 \{1 - \epsilon + \epsilon (C x + D x') \} \bar{n}_{s'} \bar{n}_{s'} \bar{n} \right] \left( \frac{\bar{n}_{s'} + 1}{\bar{n}_{s'} + 1} \right)
+ \frac{1}{2} \int dx' x'^2 \{1 - \epsilon + \epsilon (C x - D x') \} \bar{n}_{s'} \bar{n}_{s'} \bar{n} \right]
\]

where \( \omega = q c_s, x' = q/q_D, x_{\pm}'' = C x \pm D x', \bar{n}_{\pm}'' = \bar{n}(x_{\pm}''), C = c_s/c_{s''), D = c_s'/c_{s''}, \) and \( \epsilon = 1(-1) \) for N(U) processes. The first and the second terms in the above equation are contributed by class 1 events (carrier phonon jointly annihilating with another phonon to produce a third phonon) and class 2 events (carrier phonon decaying into two phonons) respectively. Integration limits for the variable \( x' \) for allowed combinations of the polarisation branch \( s', s'' \) are presented in Ref. [11]. The Grüneisen’s constant \( \gamma \) is a measure of crystal anharmonicity and our theory uses a mode-averaged value of 0.5 at room temperature [14].
3. Results and discussion
In this work we present results of our calculations of the thermal conductivity of the oxygen contaminated AlN sample, by accounting for the role of point impurities as outlined by Harris et al. [9], with an additional possibility of V\(_{\text{Al}}\)-O\(_{\text{N}}\) acting as a small-sized extended defects. The following parameters of bulk AlN has been utilised: transverse and longitudinal acoustic phonon speeds as \(c_{TA} = 4.85 \times 10^3 \text{ms}^{-1}\) and \(c_{LA} = 8.97 \times 10^3 \text{ms}^{-1}\), respectively, Debye radius \(q_D = 1.9 \times 10^{10} \text{m}^{-1}\) and the boundary length as the sample thickness.

With the reported oxygen concentration in the sample (0.29 at.%) whose thickness is 0.35 mm, our results have shown that the scattering of phonons from oxygen-related extended defects is ineffective at room temperature when the sample is under exposure to UV irradiation. However, it is found that the cross section of the phonon scattering from oxygen-related point impurity increases by 17% upon UV irradiation of the sample at room temperature and to account for the experimentally observed drop in the thermal conductivity of the sample from 223 W/m.K (before UV irradiation) to 216 W/m.K. When removing UV and substituting it with visible light, the trapped carriers are liberated and go back to their original states after several radiative recombinations. Thus, the phonon scattering rate decreases and, therefore, the thermal conductivity rises to its value before UV illumination.

Harris et al. [9] reported a drop of 8 W/m K in the thermal conductivity of AlN sample with 0.29 at.% oxygen concentration and 200 \(\mu\)m thickness upon UV illumination at \(T = 295\) K. They have proposed the following simple relationship between average thermal resistivity \(W(L)\) and sample thickness \(L\)

\[
W(L) = W_{\text{dark}} + \Delta W_{\text{uv}}(L) = W_{\text{dark}} + \frac{W_{\text{ex}}(y = 0)}{\alpha L}(1 - e^{-\alpha L}),
\]

where \(W_{\text{dark}}\) is the thermal resistivity before UV illumination, \(W_{\text{ex}}(y = 0)\) is the thermal resistivity due to excited defect centres at the sample UV illuminated surface, \(\alpha\) is the absorption coefficient, and \(y\) is the distance into the sample from the UV illuminated surface.

Using the above relationship and utilising our results for the thermal conductivity of the sample of 200 \(\mu\)m thickness and with 0.29 at.% oxygen concentration, we express the population of excited defects centres at the sample UV illuminated surface at \(T = 295\) K as follows

\[
W_{\text{ex}}(y = 0) = \frac{1}{\kappa_{\text{dark}}(1 - e^{-\alpha L})} \left( \frac{\kappa_{\text{dark}}}{\kappa_{\text{uv}}} - 1 \right),
\]

where \(\kappa_{\text{dark}}\) and \(\kappa_{\text{uv}}\) are the thermal conductivity of the sample before and upon UV illumination respectively. Using the measured absorption coefficient \(\alpha = 65 \text{ cm}^{-1}\) at wavelength 253.7 nm [9], we found \(W_{\text{ex}}(y = 0) = 0.03 \text{ cmK/W}\). This can be compared with the value of 0.03 cm K/W considered as an adjustable free parameter in the work by Harris et al. [9]. Since \(W_{\text{ex}}(y) \propto n_{\text{ex}}(y)\) and therefore \(W_{\text{ex}}(y = 0) \propto n_{\text{ex}}(y = 0)\), we can write: \(n_{\text{ex}}(y = 0) = \frac{W_{\text{ex}}(y = 0)\kappa_{\text{uv}}}{\alpha L} - 1\), where \(N_{\text{VA}}\) is the number density of aluminium vacancies. From this we estimated the number density of the defect excited centres at the sample illuminated surface to be of the order of \(2.54 \times 10^{18} \text{cm}^{-3}\). This compares with an estimate of \(1.4 \times 10^{18} \text{cm}^{-3}\) made by Harris et al. We believe that the difference between the present estimate and that by Harris et al for the defect density is due to the use of a simplified and less rigorous treatment of three-phonon scattering in the work by Harris et al.

Our estimates of \(W_{\text{ex}}(y = 0)\) and \(n_{\text{ex}}(y = 0)\) are firmly rooted in our theory of thermal conductivity, rather than the approximation scheme employed by Harris et al.. Since the role of the UV illumination is to enhance point defect scattering, we can assume the linearity relation \(n_{\text{ex}} \propto \Delta A\), where \(A_{\text{eff}}(L) = A + \Delta A(L)\) is the increased point-defect scattering parameter.
Table 1. Increase in phonon scattering cross section in UV illuminated AlN samples (with 0.29 at.% of oxygen) of different thicknesses.

| L (mm) | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 |
|--------|-----|-----|-----|-----|-----|-----|
| (∆A(L)/A) × 100% | 21.6 | 18.8 | 12.5 | 10  | 8.5 | 4.9 |

Following the previous discussion, therefore, we can write the following expression for the extra defect scattering parameter \( \Delta A(L) \) for the sample length \( L \)

\[
\Delta A(L) = \frac{A_{ex}(y = 0)}{\alpha L} \left(1 - e^{-\alpha L}\right),
\]

with \( A_{ex}(y = 0) \) considered as a fitted free parameter. Using our theory, we estimated the increase in the phonon point impurity scattering cross section \( \Delta A(L) \) due to UV illumination of AlN sample with different thicknesses (and oxygen concentration of 0.29 at.% at room temperature. These estimates are presented in Table 1. From these results we further estimate the parameter \( A_{ex}(y = 0) \) to be approximately \( 1.0 \times 10^{-46} \) s\(^3\). The results show that the change (increase) in the phonon scattering cross section due to UV irradiation decreases with the increase in the sample thickness, implying that smaller population of defect centres get excited upon UV illumination of their samples.

4. Summary
The role of UV illumination on changes in the room-temperature thermal conductivity of an AlN sample with an oxygen concentration of 0.29 at.% has been examined by applying the Callaway theory in its full form and by using a detailed account of three-phonon scattering processes. It is found that extended defects originating from oxygen incorporation play an ineffective role. The most important role of defect complexes involving Al vacancies and substitutional O is to scatter phonons in the form of point defects. It is found that for a given UV source the point defect scattering cross section depends on the sample thickness. A successful fitting of the drop in the conductivity at room temperature obtained by Harries et al. allows us predict a decrease in the percentage increase of the cross section with increase in sample thickness. The increase in the cross section decreases from 22% for the sample thickness of 0.2 mm to 5% for the sample thickness of 0.7 mm. For the sample with thickness of 200 \( \mu \)m and oxygen concentration of 0.29 at.%, we estimate the number density of the defect excited centres at the surface of the illuminated sample to be \( 2.54 \times 10^{18} \) cm\(^{-3}\).

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