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Electron/phonon coupling in group-IV transition-metal and rare-earth nitrides

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Transport electron/phonon coupling parameters and Eliashberg spectral functions $\alpha_{\text{tr}}^2 F(\hbar\omega)$ are determined for group-IV transition-metal (TM) nitrides TiN, ZrN, and HfN, and the rare-earth (RE) nitride CeN using an inversion procedure based upon temperature-dependent ($4 < T < 300$ K) resistivity measurements of high-crystalline-quality stoichiometric epitaxial films grown on MgO(001) by magnetically-unbalanced reactive magnetron sputtering. Transport electron/phonon coupling parameters λ_{tr} vary from 1.11 for ZrN to 0.82 for HfN, 0.73 for TiN, and 0.44 for CeN. The small variation in λ_{tr} among the TM nitrides and the weak coupling in CeN are consistent with measured superconducting transition temperatures 10.4 (ZrN), 9.18 (HfN), 5.35 (TiN), and < 4 K for CeN. The Eliashberg spectral function describes the strength and energy spectrum of electron/phonon coupling in conventional superconductors. Spectral peaks in $\alpha_{\text{tr}}^2 F(\hbar\omega)$, corresponding to regions in energy-space for which electrons couple to acoustic $\hbar\omega_{\text{ac}}$ and optical $\hbar\omega_{\text{op}}$ phonon modes, are centered at $\hbar\omega_{\text{ac}} = 33$ and $\hbar\omega_{\text{op}} = 57$ meV for TiN, 25 and 60 meV for ZrN, 18 and 64 meV for HfN, and 21 and 39 meV for CeN. The acoustic modes soften with increasing cation mass; optical mode energies remain approximately constant for the TM nitrides, but are significantly lower for the RE nitride due to a lower interatomic force constant. Optical/acoustic peak-intensity ratios are 1.15 ± 0.1 for all four nitrides, indicating similar electron/phonon coupling strengths $\alpha_{\text{tr}}(\hbar\omega)$ for both modes. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4832778>]

I. INTRODUCTION

Superconductivity, the ability to conduct electrons without resistance, occurs in a variety of materials. One of the earliest conventional superconductors discovered to have a relatively high transition temperature (T_c) is the group-V NaCl-structure transition-metal (TM) nitride NbN with $T_c = 16$ K.¹ Since then, conventional superconductors have found a broad range of device applications including micro-resonator detectors,^{2,3} waveguide resonators,⁴ accelerator cavities,⁵ coil magnets,⁶ qubit computing,⁷ Josephson junctions in quantum interference devices,⁸ hot electron bolometers,⁹ single-photon detectors,¹⁰ and THz mixers.¹¹

Recently, there has been increased interest in group-IV TM nitrides.^{12–15} Here, we present a systematic investigation of the transport Eliashberg coupling function $\alpha_{\text{tr}}^2 F(\hbar\omega)$, an energy-resolved measure of the electron/phonon coupling strength $\alpha_{\text{tr}}(\hbar\omega)$ and the phonon density-of-states $F(\hbar\omega)$, for the epitaxial TM nitrides TiN, ZrN, and HfN, as well as the group-IV rare-earth (RE) nitride CeN. Apart from a geometric factor which favors backscattered electrons,¹⁵ the transport Eliashberg function contains, together with the Coulomb pseudopotential μ^* ,¹⁶ all information pertaining to phonon-mediated superconductivity. As a result, properties such as temperature- and frequency-dependent energy gaps are readily acquired from $\alpha_{\text{tr}}^2 F(\hbar\omega)$ through the Eliashberg gap equations.^{17,18}

We obtain $\alpha_{\text{tr}}^2 F(\hbar\omega)$ from an inversion procedure based on temperature-dependent resistivity measurements, between

4 and 300 K, of high-crystalline-quality stoichiometric epitaxial TiN, ZrN, HfN, and CeN layers grown on MgO(001). For all compounds, the coupling strength $\alpha_{\text{tr}}^2 F(\hbar\omega)$ is determined to be approximately uniform over energy $\hbar\omega$, indicating that $\alpha_{\text{tr}}^2 F(\hbar\omega)$ effectively probes the phonon density-of-states. This is, to our knowledge, the first experimental determination of $\alpha_{\text{tr}}^2 F(\hbar\omega)$ for TiN, HfN, and CeN.

II. EXPERIMENTAL PROCEDURE

Single-crystal stoichiometric TiN, ZrN, HfN, and CeN layers, with metal/nitrogen ratios $\text{Me/N} = 1.00 \pm 0.03$ and thicknesses $t \geq 70$ nm, are grown on MgO(001) in a load-locked ultra-high-vacuum (UHV) magnetically-unbalanced stainless-steel dc magnetron sputter deposition system described in detail by Petrov *et al.*¹⁹ The composition and structure of as-deposited samples are determined using a combination of Rutherford backscattering spectrometry (RBS), high-resolution x-ray diffraction (HR-XRD), and cross-sectional transmission electron microscopy (XTEM). Details regarding film growth and characterization are described in Ref. 19 for TiN, Ref. 20 for ZrN, Ref. 21 for HfN, and Ref. 22 for CeN. All films have the NaCl structure and grow with a cube-on-cube epitaxial relationship to the substrate, $(001)_{\text{nitride}} \parallel (001)_{\text{MgO}}$ and $[100]_{\text{nitride}} \parallel [100]_{\text{MgO}}$. Relaxed lattice constants are 0.4240 (TiN), 0.4574 (ZrN), 0.4524 (HfN), and 0.5021 nm (CeN). In-plane $\xi_{\parallel}$ and out-of-plane $\xi_{\perp}$ x-ray coherence lengths are 86 and 142 nm for TiN, 18 and 161 nm for ZrN, 22 and 185 for HfN, and 7 and

26 nm for CeN. The results indicate that the films are of high crystalline quality with low mosaicity.²³

Temperature-dependent resistivities between 4 and 300 K are obtained using a Quantum Design physical property measurement system. Electrical contacts are fabricated in an FEI Strata DB-235 focused ion-beam system by Ga⁺ ion-etching four 2- μ m-diameter holes, in the van der Pauw geometry,²⁴ and then filling the holes with Pt without breaking vacuum. All contacts are tested for ohmic behavior. Current and voltage measurements are iterated through different contact pairs to account for geometric effects.

III. RESULTS AND DISCUSSION

Temperature-dependent resistivities $\rho(T)$ between 4 and 300 K are plotted in Figure 1. Room-temperature resistivity $\rho_{300\text{K}}$ values are 12.9 (TiN), 12.0 (ZrN), 14.2 (HfN), and 69 $\mu\Omega\text{-cm}$ (CeN); all essentially equal to, or better, than corresponding values for bulk crystals: 11.07 (TiN), 11.52 (ZrN), and 33 $\mu\Omega\text{-cm}$ (HfN).^{25,26} We are unaware of published results for bulk CeN. $\rho_{300\text{K}}$ values for polycrystalline films are typically ~ 2 to 10^6 times higher; $\rho_{300\text{K}}$ for polycrystalline TiN ranges from 20 to 200 $\mu\Omega\text{-cm}$,^{27,28} polycrystalline ZrN from 23 to 2000 $\mu\Omega\text{-cm}$,^{29–31} polycrystalline HfN from 225 to 800 $\mu\Omega\text{-cm}$,³² and polycrystalline CeN from 460 to $> 2 \times 10^8$ $\mu\Omega\text{-cm}$.^{33–35} The low resistivity values of our epitaxial films are an additional indicator of high structural quality.

The resistivity of all films increases approximately linearly with temperature between 100 and 300 K, indicating metallic conduction with a carrier mobility that is controlled by phonon scattering. Over this range, the temperature coefficients of resistivity, defined as $\text{TCR} = (\rho_{300\text{K}} - \rho_{100\text{K}})/\Delta T$, are 5.0×10^{-8} for TiN, 5.6×10^{-8} for ZrN, 4.0×10^{-8} for HfN, and 16.0×10^{-8} $\Omega\text{-cm K}^{-1}$ for CeN.

At temperatures T below 30 K, phonon scattering is negligible and the resistivity is primarily determined by defect and impurity scattering. Figure 1 shows that $\rho(T)$ for the four nitrides saturates at residual resistivities $\rho_0 = 2.08$ (TiN), 0.78 (ZrN), 3.5 (HfN), and 29 $\mu\Omega\text{-cm}$ (CeN). In metallic conductors, the residual resistivity ratio $\text{RRR} = \rho_{300\text{K}}/\rho_0$ is used as a metric of crystalline quality. For the group-IV nitrides under

investigation, RRR values are relatively high: 6.2 (TiN), 15 (ZrN), 4 (HfN), and 2.4 (CeN). As a result, scattering events are independent and the resistivity over the entire measured temperature range is described by Matthiessen's rule $\rho(T) = \rho_0 + \rho_{\text{ph}}(T)$, in which $\rho_{\text{ph}}(T)$ is the phonon-scattering contribution to resistivity.

Within the relaxation time approximation, $\rho_{\text{ph}}(T)$ can be expressed as³⁶

$$\rho_{\text{ph}}(T) = \frac{4\pi}{\omega_p^2 \langle \tau \rangle} = \frac{m^*}{ne^2 \langle \tau \rangle}. \quad (1)$$

ω_p is the unscreened plasma frequency and n , e , and m^* are the electron concentration, charge, and effective mass, respectively. The rate $\langle \tau \rangle^{-1}$ at which electrons scatter from phonons is given by:³⁷

$$\langle \tau \rangle^{-1} = \pi \int_0^{\hbar\omega_{\text{max}}} \frac{\hbar\omega}{k_B T} \text{csch}\left(\frac{\hbar\omega}{2k_B T}\right) \alpha_{\text{tr}}^2(\hbar\omega) F(\hbar\omega) d\hbar\omega, \quad (2)$$

in which k_B is the Boltzmann constant, $\alpha_{\text{tr}}^2(\hbar\omega)$ is the square of the transport electron/phonon coupling function, $F(\hbar\omega)$ is the phonon density-of-states, and $\hbar\omega_{\text{max}}$ is the energy of the highest phonon mode. The product $\alpha_{\text{tr}}^2(\hbar\omega) F(\hbar\omega)$ is the transport Eliashberg spectral function.³⁸

In the high-temperature limit ($\theta_D/T \ll 10$; the Debye temperature θ_D for metal nitrides ranges from 400 to 600 K (Ref. 26)), scattering is elastic³⁹ and the scattering rate reduces to¹⁶

$$\langle \tau \rangle^{-1} = \frac{2\pi k_B T}{\hbar} \lambda_{\text{tr}}. \quad (3)$$

Thus, ρ increases linearly with temperature T at a rate proportional to the transport electron/phonon coupling parameter λ_{tr} (Ref. 51) and inversely proportional to the square of the unscreened plasma frequency ω_p (see Eq. (1)). In order to determine λ_{tr} , the plasma frequency ω_p is obtained from first principles density functional theory (DFT) band-structure calculations⁴⁰ by integrating $v(k)$, the group velocity of electrons at state k , over the Brillouin zone using the relationship⁴¹

$$\omega_p^2 = \frac{e^2}{\pi^2 \hbar} \int dk \nabla_k v(k) f(k), \quad (4)$$

in which $f(k)$ is the Fermi-Dirac occupation probability function.

For the group-IV TM nitrides, we obtain ω_p values which increase with the cation atomic number Z from 7.7 for TiN to 8.9 for ZrN and 9.1 eV for HfN; for the rare-earth (RE) nitride CeN, $\omega_p = 3.3$ eV, less than half the average ω_p value of the nitrides. The transport electron/phonon coupling parameters λ_{tr} are obtained from Eqs. (1) and (3), combined with the measured TCR values, as 0.73 (TiN), 1.11 (ZrN), 0.82 (HfN), and 0.44 (CeN). The small variation in λ_{tr} among the TM nitrides and the weak coupling in CeN are consistent with superconducting transition temperatures which range from 10.4 K for ZrN to 9.18 K for HfN and 5.35 K for TiN; superconductivity is not observed above 4 K for CeN.

FIG. 1. Temperature-dependent resistivity $\rho(T)$ of single-crystal TiN, ZrN, HfN, and CeN layers grown on MgO(001) by magnetically-unbalanced reactive magnetron sputtering. TiN data from Ref. 19, ZrN from Ref. 20, HfN from Ref. 21, and CeN from Ref. 22.

The transport Eliashberg spectral functions for TiN, ZrN, HfN, and CeN are developed by first discretizing the integral in Eq. (2) into a geometric series of superimposed Einstein modes⁴²

$$\rho_{\text{ph}}(T) = \frac{4\pi m^*}{ne^2} \sum_k \alpha^2 F(\hbar\omega_k) \frac{x_k e^{x_k}}{(e^{x_k} - 1)^2}, \quad (5)$$

in which $x_k = \hbar\omega_k/k_B T$, and fitting $\rho(T)$ to Matthiessen's rule using the largest number of Einstein components at spacings ω_{k-1}/ω_k which preserve convergence stability, $\omega_{k-1}/\omega_k \geq 1.57$. The procedure is illustrated graphically in Figure 2, which shows the ZrN temperature-dependent resistivity $\rho(T)$ between 10 and 300 K multiplied by a factor of $1/T$ (dotted red curve) in order to highlight resistivity contributions due to defect and phonon scattering. The normalized residual-resistivity ρ_o/T (dashed black line) simply decays as $1/T$, while normalized Einstein components, corresponding to electron/phonon scattering, increase with temperature (black solid lines). Multiple Einstein modes are necessary to reproduce the experimental $\rho(T)$ curve. The calculated normalized temperature-dependent resistivity, which includes the normalized residual resistivity ρ_o/T and normalized phonon contributions from each of the Einstein modes, is plotted in Figure 2(a) as the orange solid line. Residuals R from a typical $\rho(T)$ fit for ZrN are shown in Figure 2(b); the agreement is excellent to within experimental uncertainty.

Transport Eliashberg spectral functions $\alpha_{\text{tr}}^2 F(\hbar\omega)$ are generated from 200 fits, including the orange $\rho(T)/T$ curve shown in Figure 2, which consist of approximately ten Einstein modes each using different starting values for $\hbar\omega_1$, the energy of the first Einstein mode. The energies of the remaining modes, for a particular fit, are defined by $\hbar\omega_1$ following the

FIG. 2. (a) Measured temperature-dependent resistivity $\rho(T)$ of epitaxial ZrN/MgO(001) multiplied by a factor of $1/T$ (red dotted line) to highlight contributions due to defect and phonon scattering. The black dashed line is the normalized residual resistivity, ρ_o/T . Each solid black line corresponds to a normalized Einstein mode of known amplitude and energy. The solid orange curve is the calculated total normalized ZrN resistivity $\rho(T)/T$, for which $\rho(T) = \rho_o + \rho_{\text{ph}}(T)$. (b) Residuals R , the difference between measured and calculated resistivities, as a function of temperature T .

stability criteria $\omega_{k-1}/\omega_k = 1.57$. Each Einstein mode contributes a discrete point, with coordinates specified by the mode's amplitude and energy, to the spectral function. As a result, 200 fits, with ten Einstein modes each, yield 2000 data points, thus resulting in a transport spectral function curve which is quasi-continuous. $\alpha_{\text{tr}}^2 F(\hbar\omega)$ for TiN, ZrN, HfN, and CeN, obtained as described above, are plotted in Figure 3 as a function of vibrational energy $\hbar\omega$. The intensity of $\alpha_{\text{tr}}^2 F(\hbar\omega)$ at a given energy $\hbar\omega$ corresponds to the population of phonon modes at that energy weighted by $\alpha_{\text{tr}}^2(\hbar\omega)$, the square of their interaction strengths with electrons.

The CeN transport Eliashberg spectral function $\alpha_{\text{tr}}^2 F(\hbar\omega)$ exhibits features centered at 21 ± 2 and 40 ± 3 meV, indicating that electrons in CeN scatter primarily from two groups of phonons. The lower-energy peak stems from electron/acoustic-phonon scattering and the higher-energy peak from electron/optical-phonon scattering. While this is the first experimental report of phonon behavior in CeN, DFT calculations⁴³ indicate that peaks in $F(\hbar\omega)$, corresponding to acoustic and optical phonon modes, occur at 21 and 39 meV, in excellent agreement with the two features observed here.

The ZrN and HfN transport Eliashberg spectral functions also exhibit two features each, corresponding to acoustic and optical phonon scattering. For ZrN, the peaks are centered at energies $\hbar\omega_{\text{ac}} = 25 \pm 2$ and $\hbar\omega_{\text{op}} = 60 \pm 6$ meV; for HfN, at $\hbar\omega_{\text{ac}} = 18 \pm 2$ and $\hbar\omega_{\text{op}} = 64 \pm 6$ meV. These results are consistent with vibrational energies obtained from ZrN and HfN Raman spectroscopy ($\hbar\omega_{\text{ac}} = 21$ and $\hbar\omega_{\text{op}} = 62$ meV for ZrN⁴³ and $\hbar\omega_{\text{ac}} = 17$ and $\hbar\omega_{\text{op}} = 65$ meV for HfN⁴⁴) as well as from neutron scattering measurements ($\hbar\omega_{\text{ac}} = 25$ and $\hbar\omega_{\text{op}} = 65$ meV for ZrN (Ref. 45) and $\hbar\omega_{\text{ac}} = 18$ and $\hbar\omega_{\text{op}} = 62$ meV for HfN (Ref. 46)).

For TiN, we obtain a single broad feature centered at ~ 42 meV, which is well fit with two Gaussian functions yielding a low-energy peak at $\hbar\omega_{\text{ac}} = 33 \pm 5$ meV and a higher-energy peak at $\hbar\omega_{\text{op}} = 57 \pm 13$ meV. These findings are in reasonable agreement with those from Raman measurements, for which $\hbar\omega_{\text{ac}} = 32$ and $\hbar\omega_{\text{op}} = 68$ meV,⁴⁸

FIG. 3. Transport Eliashberg spectral functions $\alpha_{\text{tr}}^2 F(\hbar\omega)$, obtained from temperature-dependent ($4 \leq T \leq 300$ K) resistivity measurements using an inversion procedure, for single-crystal TiN, ZrN, CeN, and HfN layers grown on MgO(001) substrates. The TiN spectrum is fit with two Gaussian functions (dashed lines). The lower-energy peak in each spectrum arises from electron/acoustic-phonon coupling while the higher-energy peak is from electron/optical-phonon coupling.

and neutron scattering experiments, $\hbar\omega_{ac}=37$ and $\hbar\omega_{op}=74$ meV.⁴⁹

In binary compounds, each atom within the primitive unit cell contributes three phonon modes (one for each degree of freedom) to the phonon density-of-states $F(\hbar\omega)$ such that the total density of normal modes, for a large number N of unit cells, is $6N$. Compounds composed of atoms with significant mass differences exhibit two groups of phonons: the lower-energy group corresponds to acoustic phonon modes and the higher-energy group to optical phonon modes. The acoustic-mode energy is primarily determined by the mass of the heavier element. For longitudinal modes at the [001] zone boundaries, where van Hove singularities give rise to a large contribution to $F(\hbar\omega)$,⁴⁵ the acoustic phonon energy $\hbar\omega_{ac}=\hbar(2C/m_{Me})^{1/2}$, in which m_{Me} is the mass of the metal atom and C is a material-dependent interatomic force constant.⁴⁶ The softening of $\alpha_{tr}^2F(\hbar\omega)$ acoustic modes in Figure 3 from TiN to ZrN to CeN to HfN, and the corresponding increase in the energy separation between acoustic and optic mode positions, results primarily from increases in the cation atomic mass: $m_{Ti}=47.9$, $m_{Zr}=91.2$, $m_{Ce}=140.1$, and $m_{Hf}=178.5$ amu.

The energy of the optical mode, $\hbar\omega_{op}=\hbar(2C/m_N)^{1/2}$, is governed by the mass of the lighter element ($m_N=14$ amu). For the TM nitrides, we obtain interatomic force constants C which are within 25% of each other: $C=87$ (TiN), 97 (ZrN), and 110 N·m⁻¹ (HfN). For the RE nitride CeN, however, $C=41$ N·m⁻¹, less than half the average TM nitride C value, 96 N·m⁻¹. This is consistent with the fact that the cohesive energy E_{coh} of CeN, 12.81 eV/formula-unit,⁴⁷ is significantly less than that of the TM nitrides: 14.34 for TiN,⁴⁸ 15.04 for ZrN,⁴⁹ and 15.22 eV/formula-unit for HfN.⁵⁰

Measured optical/acoustic $\alpha_{tr}^2F(\hbar\omega)$ peak intensity ratios I_{op}/I_{ac} are 1.2 ± 0.1 (TiN), 1.12 ± 0.05 (ZrN), 1.11 ± 0.05 (HfN), and 1.18 ± 0.05 (CeN). Tunneling spectroscopy measurements¹² and *ab initio* $\alpha^2F(\hbar\omega)$ calculations¹⁵ for ZrN are in good agreement with $I_{op}/I_{ac}=1.25$. For binary compounds with equal acoustic and optical phonon densities and an energy-independent coupling strength $\alpha_{tr}^2F(\hbar\omega)$, $I_{op}/I_{ac}=1$. The proximity of our measured I_{op}/I_{ac} ratios to unity demonstrates that $\alpha_{tr}^2(\hbar\omega)$ is approximately constant over $\hbar\omega$; thus, the transport Eliashberg spectral function provides, for the compounds investigated here, an effective measurement of the phonon density-of-states.

IV. CONCLUSIONS

We have determined the transport electron/phonon coupling parameters λ_{tr} and Eliashberg spectral functions $\alpha_{tr}^2F(\hbar\omega)$ for stoichiometric epitaxial group-IV TM nitrides TiN, ZrN, and HfN and the RE nitride CeN using an inversion procedure based upon temperature-dependent resistivity measurements ($4 \leq T \leq 300$ K). We find that the coupling parameter is largest for ZrN ($\lambda_{tr}=1.11$), which exhibits the highest superconducting transition temperature $T_c=10.4$ K, and smallest for CeN ($\lambda_{tr}=0.44$), which is not superconducting above 4 K. For HfN ($T_c=9.18$ K) and TiN ($T_c=5.35$ K), λ_{tr} is 0.82 and 0.73. $\alpha_{tr}^2F(\hbar\omega)$ vs. $\hbar\omega$ results for all compounds investigated indicate that the electron/phonon

coupling strength $\alpha_{tr}^2(\hbar\omega)$ is distributed approximately uniformly over energy $\hbar\omega$ and thus the group-IV nitride transport Eliashberg spectral functions provide an effective measure of the phonon density-of-states. The acoustic phonon modes soften monotonically with increasing cation mass from 33 ± 5 (TiN) to 25 ± 2 (ZrN) to 21 ± 2 (CeN) to 18 meV (HfN). The spectral $\alpha_{tr}^2F(\hbar\omega)$ peaks corresponding to optical modes in the group-IV TM nitrides remain constant at ~ 60 meV (57 ± 13 for TiN, 60 ± 6 for ZrN, and 64 ± 6 meV for HfN) and decrease to 40 ± 3 meV for the group-IV RE nitride CeN, reflecting a lower bond strength.

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