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P-type Al-doped Cr-deficient CrN thin films for thermoelectrics

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Thermoelectric properties of chromium nitride (CrN)-based films grown on c-plane sapphire by dc reactive magnetron sputtering were investigated. In this work, aluminum doping was introduced in CrN (degenerate n-type semiconductor) by co-deposition. Under the present deposition conditions, over-stoichiometry in the rock-salt structure is obtained. A p-type conduction is observed with nitrogen-rich CrN combined with aluminum doping. The Cr0.9Al0.1N1.7 film exhibited a high Seebeck coefficient and a sufficient power factor at 300 °C. These results are a starting point for designing p-type/n-type thermoelectric materials based on chromium nitride films, which are cheap and routinely grown on the industrial scale.

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E nergy-harvesting devices based on the thermoelectric (TE) effect have been driving the search for functional materials to improve the efficiency of these devices and the production cost.1–3) In the presence of a temperature gradient, a thermoelectric generator can directly convert heat into electricity. TE devices are composed of different legs of specific semiconductors connected electrically in series.4,5) The efficiency of a TE device is determined by a dimensionless figure of merit (zT) defined as zT = S2σ/k, where S, σ, T, k, and k are the Seebeck coefficient, electrical conductivity, absolute temperature, electronic thermal conductivity, and lattice thermal conductivity (phonon), respectively. In thermoelectric materials, the thermal conductivity is dominated by phonon contributions. Therefore, the maximum zT will be achieved by maximizing the power factor Sσ and minimizing the lattice thermal conductivity. Tellurium-based materials have shown the highest zT values among established thermoelectric materials.3) However, alternative materials are needed because of the scarcity, toxicity, and low global production of tellurium.6–10) In the search for thermoelectric materials with more abundant elements and nontoxic materials, silicides, oxides, nitrides, and organic materials are representative materials.2,11) Among the nitrides for thermoelectric applications, scandium- and chromium-based nitrides are interesting12–18) because ScN and CrN both exhibit n-type conduction with promising properties for further integration in TE devices. However, p-type materials are also needed. ScN can be made p-type by alloying/doping with Mg or Mn on Sc sites.10,13,19)

n-type CrN exhibits a high power factor and an intrinsically lower thermal conductivity than ScN. This material is well known and routinely used in industrial-scale production as hard coatings, showing promise for upgrading and moderate cost.12,15,20) Binary CrN has a cubic rock-salt structure susceptible to nonstoichiometry with a Schottky defect, which consists of charge-balancing cation vacancies and anion vacancies similar to other transition metal nitrides.15,21–23) The low thermal conductivity of binary CrN partly originates from its rock-salt structure, which provides a resonant bonding effect.24) Lucovsky and White demonstrated, by first-principles calculations, that a long-range interaction in that type of structure leads to acoustic phonon scattering and therefore a low thermal conductivity.25) Furthermore, the magnetic structure present in nonmagnetic CrN (rock-salt) leads to a much lower thermal conductivity for CrN than for other rock-salt transition-metal nitrides.15) The presence of vacancies and/or other defects coupled with the narrow band gap of the intrinsic material causes the charge carrier density to vary and thus allows for a wide range of electrical properties from semiconductive to metallic-like conduction properties.26,27) Several groups have reported on n-type CrN—a, which exhibits reasonable zT values (0.1–0.35) with moderate electrical conductivity (1.7–350 mΩ·cm), low thermal conductivity (2–4 W·m−1·K−1), and high absolute values of the Seebeck coefficient (135–200 µV·K−1).15,28–30) Quintela et al. reported an improvement of the thermoelectric properties of CrN by controlling the stoichiometry after an extra annealing at a high temperature under NH3.31) After annealing, stoichiometric 1:1 CrN exhibited at room temperature (RT) a Seebeck coefficient of −110 µV·K−1, a resistivity of 5 mΩ·cm, a power factor (S2σ) of 0.24 mW·m−1·K−2, and a figure of merit zT of 0.16 (for comparison, PbTe:Tl exhibited zT of 0.1 at RT).

With the aim to develop both n-type and p-type CrN-based thermoelectric materials, which will ultimately be required for devices, we demonstrate here the possibility of converting n-type CrN to p-type Cr1−xAlxN, by controlling the stoichiometry and doping with aluminum. We show the effect of Cr deficiency in the rock-salt structure as well as the effect of Al doping in this Cr-deficient CrN on the thermoelectric properties. The different characteristics of the films were examined (crystal structure, morphology, composition) as well as the thermoelectric properties evaluated from RT up to 525 °C. 330-nm-thick films of Cr-based nitrides were deposited at Tg = 600 °C on c-plane sapphire substrates using a magnetically unbalanced magnetron sputtering system with a confocal target configuration.31,32) The Cr (99.95% purity) and Al (99.9995% purity) targets were 7.5-cm-diameter water-cooled disks electrically connected to a DC power supply. Sputtering was carried out at a constant pressure of 0.34 Pa in an Ar/N2 (Ar : N2 flow ratio of 15 : 20 sccm) gas mixture. A constant power of 200 W was applied to the Cr target, and in the case of
Cr<sub>1−x</sub>Al<sub>x</sub>N<sub>y</sub>, a constant DC power of 50 W was applied to the Al target. The metallic targets were located at a distance of 18 cm from the substrate, which was mounted on a rotating sample holder coupled with a heating element. A bias voltage of −30 V (DC equivalent) was applied during deposition to the substrate using an RF power supply. Prior to deposition, the substrates were first cleaned using detergent steps, then for 10 min in an ultrasonic bath with acetone, which was repeated with ethanol, and finally blown dry with a N<sub>2</sub> gun. The detergent steps are described elsewhere.33)

The crystal structure of the films was determined by X-ray diffraction (XRD) analysis. θ–2θ scans were acquired using a PANalytical X’Pert PRO diffractometer with Cu Kα radiation and a nickel filter. Philips X’Pert-MRD with Cu Kα radiation was used for obtaining rocking curves and ϕ scans of the films.

Elemental composition was investigated by scanning electron microscopy (SEM) using JEOL-7001F-TTLS equipped with a wavelength-dispersive X-ray spectroscopy (WDS) microanalysis unit from Oxford Instruments. Measurements were acquired at 10 kV and 20 nA using the Lα line of Cr and Kα lines of N, O, and Al. The quantification was performed using INCA wave software. The morphology of the films was examined by SEM (Zeiss LEO Gemini 1550).

The in-plane Seebeck coefficient and electrical resistivity were measured simultaneously in a low-pressure helium atmosphere (~0.09 MPa, purity 99.999% with <0.5 ppm residual oxygen) using ULVAC-RIKO ZEM3 from RT up to 525 °C. The contributions of the substrate to the Seebeck coefficient and electrical resistivity are negligible, and the instrumental error is within 7%.

WDS measurements of the two films show over-stoichiometry in nitrogen. The final compositions calculated from the WDS measurements were CrN<sub>1.18</sub> and Cr<sub>0.96</sub>Al<sub>0.04</sub>N<sub>1.17</sub>. Compositions are normalized to the metal content (Cr+Al). The oxygen contamination is lower than 2 at. %.

Figure 1(a) shows the θ–2θ XRD patterns of the CrN<sub>1.18</sub> and Cr<sub>0.96</sub>Al<sub>0.04</sub>N<sub>1.17</sub> films. The two thin films exhibit a high degree of (111) orientation. Rocking curves of the main 111 peak are shown in the inset of Fig. 1(b). Figure 1(b) shows the ϕ-scans obtained from the 200 reflections measured at ψ = 54.74°. Six reflections separated from each other by 60° are observed, instead of the three normally observed on a cubic system, owing to the presence of twin domains in the cubic-superstructure, calculated from the main dihedral (12.527 Å) corresponds to that of the 3 × 3 supercell of the CrN unit cell (4.176 Å) and might be the result of vacancy ordering and/or strain induced at the substrate/film interface. Nevertheless, the two thin films were considered as being a single phase with cubic CrN structure with cell parameters of 4.176 Å for CrN<sub>1.18</sub> and 4.178 Å for Cr<sub>0.96</sub>Al<sub>0.04</sub>N<sub>1.17</sub> (calculated from the 111 diffraction peak).

Both films had an overall composition with over-stoichiometry in N and retained the CrN rock-salt cubic structure. The over-stoichiometry may be due to chromium vacancies and/or the different Cr valences from +III to +IV necessary to conserve the charge neutrality of the material.

Top-view SEM images of the two films (see Fig. 2) indicate their similar morphologies but different grain sizes. They consist of rounded and triangular grains with diameters of 20–30 and 8–16 nm for CrN<sub>1.18</sub> and Cr<sub>0.96</sub>Al<sub>0.04</sub>N<sub>1.17</sub>, respectively. At the surface, the grains tend to merge, forming elongated features.

The thermoelectric properties of the films measured from RT to 525 °C are shown in Fig. 3. The Seebeck coefficient, electrical resistivity, and power factor are plotted. The CrN<sub>1.18</sub> thin film exhibits n-type semiconductor behavior with negative Seebeck coefficients and decreasing resistivity as a function of temperature [Fig. 3(a)]. The Seebeck coeffi-

![Fig. 1.](image-url)
coefficients between \(-3\) and \(-50\) µV·K\(^{-1}\) are lower than those in the literature, where most reports describe n-type semiconductor behavior for stoichiometric (CrN) or under-stoichiometric (CrN\(_{1-\delta}\)) and Seebeck coefficients of typically around \(-200\) µV·K\(^{-1}\).\(^{15,28-30}\) The over-stoichiometry (CrN\(_{1+\delta}\)) may, as explained previously, introduce holes in the structure or a change in the valence of Cr, which explains the reduced absolute Seebeck coefficient.

The Seebeck coefficient of semiconductors can be described by the Mott-Boltzmann formalism using a relatively simple model with an energy-independent scattering approximation and a parabolic band.\(^{4}\) The Seebeck coefficients (Si) for the majority and minority charge carriers depend on the carrier concentration of electrons or holes (n or p), the effective mass (m\(^*\)), and the temperature (T):\(^{4,5}\)

\[
S_i = \frac{8\pi^2 k_B^2 T}{3e h^2} m^* (\frac{2}{3})^{2/3},
\]

where \(h\) is Planck’s constant. In doped semiconductors, either the conduction (electron) or the valence (hole) band will dominate the transport. However, in intrinsic semiconductors, both bands may play equal roles in the transport. Thus, the total Seebeck (ST) coefficient is given by\(^{5}\)

\[
S_T = \frac{S_1 \sigma_1 + S_2 \sigma_2}{\sigma_1 + \sigma_2},
\]

The two types of charge carriers (holes and electrons, corresponding to subscripts 1 and 2, respectively) would then compete and cancel out the induced Seebeck voltage. This is analogous to metals, which have low Seebeck coefficients, an extreme case being Ti\(_3\)SiC\(_2\) with \(S = 0\) over a wide temperature range.\(^{35-37}\) As observed for CrN\(_{1.18}\), a direct consequence of the presence of the two types of charge carrier in similar quantities in the material is the reduction in the absolute Seebeck coefficient to low negative values (0 to \(-50\) µV·K\(^{-1}\)) compared with the values of \(-150\) to \(-300\) µV·K\(^{-1}\) reported in the literature.\(^{15,28-30}\)

In contrast, the Cr\(_{0.96}\)Al\(_{0.04}\)N\(_{1.17}\) thin film exhibited positive Seebeck coefficients of around +140 µV·K\(^{-1}\) in the 200–350

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**Table I.** 2\(^\circ\) and d-spacing values of the diffraction peaks of the CrN\(_{1.18}\) film, the reference of the cubic CrN from ICDD data, and a possible cubic superstructure.

| Notation in Fig. 1(a) | Thin-film CrN\(_{1.18}\) cubic (4.176 Å) | CrN, reference\(^a\): cubic (4.135 Å) | Possible superstructure\(^b\): cubic (12.527 Å) |
| --- | --- | --- | --- |
| 2\(\theta\) (°) | d (Å) | hkl | 2\(\theta\) (°) | d (Å) | hkl | 2\(\theta\) (°) | d (Å) |
| — | — | — | 111 | 2.234 | 7.236 | 111 | 12.231 | 7.236 |
| A | 24.037 | 3.618 | 111 | 37.648 | 2.387 | 333 | 37.267 | 2.411 |
| 111 CrN | 37.267 | 2.411 | 222 | 80.378 | 1.944 | 444 | 50.450 | 1.809 |
| B | 50.472 | 1.808 | — | — | 555 | 63.397 | 1.447 |
| — | — | 79.539 | 1.204 | 222 | 80.378 | 1.944 | 666 | 79.473 | 1.206 |

\(^a\) ICDD.01-074-8390

\(^b\) Possible superstructure defined as 3 × 3 CrN cell (angles and d-spacings of each hkl reflection are calculated from the experimental d\(_{111}\) spacing of 2.411 Å)

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**Fig. 2.** Top-view SEM images of (a) CrN\(_{1.18}\) and (b) Cr\(_{0.96}\)Al\(_{0.04}\)N\(_{1.17}\) films grown on c-plane sapphire.

**Fig. 3.** Temperature dependence of (a) Seebeck coefficient, (b) electrical resistivity, and (c) calculated corresponding power factor of CrN\(_{1.18}\) and Cr\(_{0.96}\)Al\(_{0.04}\)N\(_{1.17}\) films grown on c-plane sapphire.
°C range, while lower values of around +100 µV·K⁻¹ were obtained at RT and 525 °C, i.e., on either side of the maximum plateau. Zhang et al. reported, for the specific case of Fe₂S₃ semiconductor thin films, some inconsistency between carrier types on the basis of positive values of S and the Hall effect measurement. In a specific case of a distorted semiconductor with a low positive Seebeck (+11 µV·K⁻¹) coefficient, n-type conduction measured on the basis of the Hall effect was also observed. In the present work, Cr₀.₉₆Al₀.₀₄N₁.₁₇ exhibited a high positive Seebeck coefficient; therefore, p-type conduction can be deduced. The absolute values of the Seebeck coefficients are comparable to those reported for the n-type semiconductor CrN (from −110 to −240 µV·K⁻¹).

The temperature dependence of the electrical resistivity of the two samples is typical for semiconductors. In both cases, the electrical resistivity decreases from around 30 mΩ·cm at RT to less than 5 mΩ·cm at 500 °C [Fig. 3(b)]. As the electrical resistivity behavior and values are similar for the two films, the difference in the calculated power factor [Fig. 3(c)] between samples with and without Al doping is governed here by the Seebeck coefficient. Because of its low Seebeck coefficient, the CrN₁.₁₈ film had a very low power factor. The Cr₀.₉₆Al₀.₀₄N₁.₁₇ film had power factor values between 0.05 mW·m⁻¹·K⁻² (at RT) and 0.37 mW·m⁻¹·K⁻² (at 500 °C). Compared with p-type TE materials, among the highest power factors can be found in p-type-SbTe films, which have a power factor of 0.78 mW·m⁻¹·K⁻² at 300 °C (S = +160 µV·K⁻¹ and ρ = 3 mΩ·cm), and p-type Ca₁₀Co₄O₉ films, which have a power factor of 0.76 mW·m⁻¹·K⁻² at 500 °C (S = +175 µV·K⁻¹ and ρ = 4 mΩ·cm).⁹,¹⁰ n-type CrN exhibited, at 500 °C, a power factor of 1.5 mW·m⁻¹·K⁻² (S = −200 µV·K⁻¹ and ρ = 2 mΩ·cm).³⁸

This study revealed an important aspect of the composition variation of CrN₁+δ. The nitrogen content in the rock-salt structure is the key to the final thermoelectric properties of the film. Over-stoichiometry of the material reduces the Seebeck coefficient of the n-type semiconductor. In the present study, the semiconductor behavior of aluminum-doped over-stoichiometric CrN₁+δ (CrAlN) showed a dramatic change to p-type and Seebeck coefficients were high. Cr₀.₉₆Al₀.₀₄N₁.₁₇ (p-type semiconductor) exhibited a high absolute Seebeck coefficient values and a power factor as high as that reported for n-type CrN₁−δ. Thus, both n-type and p-type conduction with good thermoelectric properties can be achieved in CrN thin films, where the p-type material was obtained by Al doping of the over-stoichiometric CrN₁+δ film. These materials are cheap and routinely grown on an industrial scale by PVD.

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