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Epitaxial growth and electrical transport properties of Cr₂GeC thin films

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Cr₂GeC thin films were grown by magnetron sputtering from elemental targets. Phase-pure Cr₂GeC was grown directly onto Al₂O₃(0001) at temperatures of 700–800 °C. These films have an epitaxial component with the well-known epitaxial relationship Cr₂GeC(0001)//Al₂O₃(0001) and Cr₂GeC(11 $\bar{2}$ 0)//Al₂O₃(1 $\bar{1}$ 00) or Cr₂GeC(11 $\bar{2}$ 0)//Al₂O₃(1 $\bar{2}$ 10). There is also a large secondary grain population with (10 $\bar{1}$ 3) orientation. Deposition onto Al₂O₃(0001) with a TiN(111) seed layer and onto MgO(111) yielded growth of globally epitaxial Cr₂GeC(0001) with a virtually negligible (10 $\bar{1}$ 3) contribution. In contrast to the films deposited at 700–800 °C, the ones grown at 500–600 °C are polycrystalline Cr₂GeC with (10 $\bar{1}$ 0)-dominated orientation; they also exhibit surface segregations of Ge as a consequence of fast Ge diffusion rates along the basal planes. The room-temperature resistivity of our samples is 53–66 $\mu\Omega\text{cm}$. Temperature-dependent resistivity measurements from 15–295 K show that electron-phonon coupling is important and likely anisotropic, which emphasizes that the electrical transport properties cannot be understood in terms of ground state electronic structure calculations only.

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I. INTRODUCTION

The $M_{n+1}AX_n$ phases ($n = 1-3$, or MAX phases) are a group of ternary carbides and nitrides (X) of transition metals (M) interleaved with a group 12–16 element (A) which exhibit an exciting combination of metallic and ceramic properties.¹ Up-to-date exhaustive reviews can be found in Refs. 2 and 3. Although a relatively little researched member of the MAX-phase family,^{4,5} Cr₂GeC exhibits a number of traits that render it interesting from a fundamental research point of view, such as its reported thermal expansion coefficient which is the highest of the known MAX phases.^{6,7} The high-pressure behavior of Cr₂GeC has been studied,^{8,9} and there is a recent study using perturbed angular correlation to probe the local surrounding of the atoms in Cr₂GeC.¹⁰ Furthermore, there are a few theoretical studies^{11,12} which exhibit discrepancies compared to experimental results on Cr₂GeC. For example, the calculated thermal expansion coefficient¹² is more than 30% larger than the experimental value,⁶ and the calculated density of states (DOS) at the Fermi level E_F is around 7–8 states/(eVcell),¹¹ while the experimentally determined DOS(E_F) is 22 states/(eVcell) from measurements of the heat capacity¹³ [the coefficient γ for the electronic heat capacity is proportional to DOS(E_F)].¹⁴ A similar major discrepancy was observed for Cr₂AlC and V₂AlC.^{2,15,16}

Because of these intriguing observations and the limited amount of studies available, we are interested in Cr₂GeC. For synthesis of this phase, thin film growth is a potentially important approach because of the relative ease with which numerous MAX phases can be epitaxially grown,^{2,17} often as single crystals which facilitates characterization of their electronic structure and properties.^{18,19} It may also be technologically important, e.g. for Ti₃SiC₂ contacts to SiC.^{20–22} As thin films, the close relatives of Cr₂GeC, Ti₂GeC,^{23–26} V₂GeC,^{27,28} and Cr₂AlC^{29–34} have all been investigated. From a potential technological viewpoint, the latter two are

particularly interesting since they can be grown at a relatively low substrate temperature (450 °C),^{27,29} which is essential for deposition onto technologically relevant substrates, such as steels. In a recent report, Li *et al.* showed that Cr₂AlC can be deposited even at a temperature as low as 370 °C.³³ However, thin film growth of Cr₂GeC is not explored; only a set of preliminary results are included in the Ph.D. thesis of T. H. Scabarozzi.³⁵ Although of relatively high crystalline quality as indicated by the residual resistivity ratio,³⁵ the samples contained large amounts of impurity phases, such as the inverse perovskite Cr₃GeC and the Nowotny phase Cr₅Ge₃C_x, which prevents reliable conclusions about properties.

In this paper, we report on the growth of phase-pure Cr₂GeC thin films (~ 190 nm thick) by magnetron sputter deposition at 800 °C. The films are grown epitaxially directly onto Al₂O₃(0001); there is, however, a large secondary Cr₂GeC grain populations with (10 $\bar{1}$ 3) orientation. We show that Cr₂GeC can be grown down to 500 °C but with a polycrystalline structure with (10 $\bar{1}$ 0)-dominated texture. Deposition onto Al₂O₃(0001) with TiN(111) seed layer and MgO(111) yielded growth of almost exclusively epitaxial Cr₂GeC(0001). Resistivity measurements indicate that the anisotropy in the conductivity of Cr₂GeC is substantial but relatively limited in relation to expectations from band-structure calculations but also indicate anisotropic electron-phonon coupling. These results emphasize the complexity of the anisotropy of the electronic properties of these compounds.

II. EXPERIMENTAL DETAILS

Cr-Ge-C thin films were deposited onto Al₂O₃(0001) substrates from elemental Cr (99.95% purity), Ge (99.999%), and graphite (99.999%) targets. Additional depositions were made onto Al₂O₃(0001) with a predeposited epitaxial TiN(111) seed layer and directly onto MgO(111) substrates. The substrates were ultrasonically degreased in acetone then in ethanol for

five minutes. The MgO(111) substrates were annealed in vacuum in the deposition chamber for 1 h at 800 °C prior to deposition. The sputtering gas was Ar at a pressure of ~ 0.3 Pa, and the base pressure was below 5×10^{-6} Pa. The targets (75 mm diameter) were arranged on a confocal magnetron cluster and located at a distance of 18 cm from the substrate,³⁶ which was mounted on a rotating sample holder. The Cr and C targets were run in DC power-control mode, while the Ge target was RF sputtered. The power stated is the resulting DC power. The films were deposited to a thickness of ~ 190 nm [determined by transmission electron microscopy (TEM)], corresponding to a deposition time of 30 min.

X-ray diffraction (XRD) θ - 2θ measurements and ω scans (rocking curves) were carried out in a Bruker D8 diffractometer using Cu K α radiation. For θ - 2θ measurements, the incidence angle was slightly offset (typically 0.4°) so as to reduce the Al₂O₃ 0006 peak and eliminate secondary diffraction features, i.e. the Cu K β and W L α artifacts as well as diffraction of bremsstrahlung (e.g. Fig. 4 in Ref. 37). This offset has a marginal effect on the diffraction pattern from the films, as verified by a selected set of control measurements, both without offset and with offset aligned to maximize the Al₂O₃ 0006 peak.

Time-of-flight elastic recoil detection analysis (ToF-ERDA) was used to obtain elemental depth profiles of the as-deposited films. The measurements were performed with a 40 MeV ¹²⁷I⁹⁺ ion beam using the setup at Uppsala University.³⁸ The recoil angle was 45°, while the incident angle of primary ions and the exit angle of recoils were both set to 67.5° relative to the surface normal. All spectra were analyzed using the CONTES code³⁹ to obtain relative atomic concentration profiles from the recoil energy of each element.

Atomic force microscopy (AFM) imaging was performed in tapping mode using a Dimension 3100 AFM from BRÜKER and processed with the analysis software WSxM.⁴⁰ Scanning electron microscopy (SEM) in secondary-electron imaging mode was performed on an LEO 1550 SEM operating at 10 kV. Transmission electron microscopy (TEM) was performed on a JEOL 2200FS operating at 200 kV. Cross-sectional samples for TEM were mechanically thinned down to 10 μ m by tripod polishing. Ion milling was then applied using a Gatan precision ion polishing system (PIPS) with a 2.5 keV Ar⁺ ion beam at 8° of incidence with respect to the surface of the sample. Once electron transparency was reached, a final ion milling step was applied with lower angle (4°) ion beams.

The room-temperature (RT) resistivity of selected films was measured by a standard four-point probe setup. Measurements of the resistivity in the temperature range of 15–295 K were carried in a Van der Pauw geometry for two samples, one with preferred (10 $\bar{1}$ 3) orientation (cf. Fig. 1 and Sec. III A) and the second fully (000 ℓ)-oriented, with a small amount of Cr₂₃C₆ impurity (cf. Fig. 9, second from bottom).

The band structure of Cr₂GeC was calculated with the WIEN2K code,⁴¹ a linearized augmented plane wave approach based on the density functional theory (DFT). Calculations were performed within the generalized gradient approximation, in a nonspin-polarized configuration. The basis set convergence was $R(k_{\max}) = 8$, and a mesh of 1500 k points in the full Brillouin zone was used. The calculated lattice parameters are $a = 2.902$ Å and $c = 11.826$ Å; relatively close

FIG. 1. θ - 2θ x-ray diffractogram of phase-pure Cr₂GeC grown at a substrate temperature of 800 °C with target powers of 60 W for Cr, 50 W for Ge, and 260 W for C. Inset: pole figure of the Cr₂GeC 0006 peak.

to the experimental values of 2.95 Å and 12.08 Å, respectively.¹ Further, the calculated band structure is very similar to that of Bouhemadou,¹¹ who employed a pseudopotential plane wave approach and the local density approximation, indicating the reliability of the calculated band structure.

III. RESULTS

A. Phase-pure Cr₂GeC thin films

Figure 1 shows a θ - 2θ x-ray diffractogram of an optimized sample of phase-pure Cr₂GeC grown at a substrate temperature of 800 °C with target powers of 60 W for Cr, 50 W for Ge, and 260 W for C. The inset is a pole figure of the Cr₂GeC 0006 peak (see below). The Cr₂GeC diffraction peaks are at 2θ positions of 14.64°, 29.51°, 41.89°, and 44.88°, corresponding to the 0002, 0004, 10 $\bar{1}$ 3, and 0006 peaks, virtually at their exact positions according to the structure factor. The 10 $\bar{1}$ 3/000 ℓ peak-intensity ratio is somewhat higher than according to the structure factor, indicating preferred (10 $\bar{1}$ 3) orientation, which is corroborated by TEM results below. Since the measurement was aligned to eliminate diffraction from the substrate, we can exclude that there could be a contribution from the Al₂O₃ 0006 peak. For brevity, we will refer to this as (10 $\bar{1}$ 3)-oriented films in the remainder of this article. For the 000 ℓ peaks of this sample, rocking curve (not shown) full widths at half maximum (FWHM) were relatively large, $\sim 1.4^\circ$, indicating mosaicity. The composition of this film determined by ERDA (cf. Sec. III B) is Cr:Ge:C = 0.51:0.24:0.25 (O < 0.001) or 2:1:1 within the uncertainty of the technique.

Figure 2 shows θ - 2θ x-ray diffractograms of Cr₂GeC films deposited (using the same deposition parameters as for the film in Fig. 1) onto an Al₂O₃(0001) substrate with a predeposited TiN(111) seed layer and onto an MgO(111) substrate. In both cases, 000 ℓ rocking curve FWHM (not shown) were $\sim 1.4^\circ$, indicating that the crystalline quality is very similar to the samples deposited directly onto Al₂O₃(0001), even though the lattice mismatch is lower; 1.6% for TiN(111), assuming that

FIG. 2. θ - 2θ x-ray diffractograms of Cr_2GeC films deposited (with the same deposition parameters as the film in Fig. 1) onto an $\text{Al}_2\text{O}_3(0001)$ substrate with a predeposited $\text{TiN}(111)$ seed layer and onto an $\text{MgO}(111)$ substrate.

the TiN is fully relaxed; and 0.6% for $\text{MgO}(111)$, compared to 9% for $\text{Al}_2\text{O}_3(0001)$. In contrast, in Fig. 2, the 000ℓ peaks are dominant with a relatively small $10\bar{1}3$ peak; unlike in Fig. 1, where the $10\bar{1}3$ peak is stronger than the 0006 peak. Therefore, the orientation distribution of the Cr_2GeC differs depending on substrate. These results, together with pole figures (not shown) of the Cr_2GeC 0006 and $10\bar{1}3$ peaks, show that, as expected, the Cr_2GeC is epitaxially grown onto the $\text{Al}_2\text{O}_3(0001)$ substrate. The epitaxial relationship is the well-known $\text{Cr}_2\text{GeC}(0001)//\text{Al}_2\text{O}_3(0001)$ and $\text{Cr}_2\text{GeC}(11\bar{2}0)//\text{Al}_2\text{O}_3(1\bar{1}00)$ or $\text{Cr}_2\text{GeC}(11\bar{2}0)//\text{Al}_2\text{O}_3(\bar{1}2\bar{1}0)$.^{17,42,43} However, for films grown directly onto $\text{Al}_2\text{O}_3(0001)$, a sixfold contribution at an azimuth angle of 60° was also observed (see inset in Fig. 1), showing the existence of a large secondary epitaxial grain population with $(10\bar{1}3)$ out-of-plane orientation (cf. TEM below). For films grown onto $\text{MgO}(111)$ or $\text{TiN}(111)/\text{Al}_2\text{O}_3(0001)$, this sixfold contribution was not observed. Although a small amount of diffracted intensity from $(10\bar{1}3)$ planes oriented parallel to the surface could be detected in θ - 2θ scans, their contribution is too weak to be clearly seen in the pole figures. Given that the $10\bar{1}3/0006$ peak-intensity ratio is ~ 6 for a randomly oriented polycrystal, but less than 0.1 in Fig. 2, these results show that the samples deposited onto $\text{MgO}(111)$ or $\text{TiN}(111)/\text{Al}_2\text{O}_3(0001)$ are almost exclusively epitaxial $\text{Cr}_2\text{GeC}(0001)$.

In Fig. 2, the 2θ positions of the 000ℓ peaks are the same irrespective of substrate (14.64 , 29.51 , and 44.89 for 0002 , 0004 , and 0006 , respectively) and essentially identical to the peak positions for the films deposited directly onto $\text{Al}_2\text{O}_3(0001)$. The positions of the $10\bar{1}3$ peak, however, are 41.93° for the film deposited onto $\text{TiN}(111)$ and 41.83° for the film deposited onto $\text{MgO}(111)$, suggesting differences in macrostrains.

Figure 3 shows TEM images of a phase-pure Cr_2GeC sample whose composition is identical to the one of the previously presented samples (Figs. 1 and 2). Figure 3(a) is an overview image and 3(b) the corresponding selected

FIG. 3. (Color online) (a) Bright field micrograph and (b) SAED pattern of phase-pure Cr_2GeC grown at a substrate temperature of 800°C (cf. Fig. 1). (c)–(e) Dark field micrographs of the film illustrating (c) the basal plane growth initiated on the substrate and (d) and (e) the subsequent nucleation of $(10\bar{1}3)$ grains.

area electron diffraction (SAED) pattern. Figures 3(c)–3(e) are dark-field micrographs of the film illustrating (c) the basal plane growth initiated on the substrate and (d) and (e) the subsequent nucleation of grains with planes of the $(10\bar{1}3)$ family oriented parallel to the surface. Figures 4(a) and 4(b) are high-resolution images acquired near the substrate. As can be seen, the Cr_2GeC is initially epitaxially grown onto the $\text{Al}_2\text{O}_3(0001)$ substrate [Fig. 4(a)]. Nucleation of nonbasal-oriented [$(10\bar{1}3)$ -oriented] grains has occurred in some sites within ~ 20 nm of the substrate, as seen in Fig. 4(b). For this last sample, the $(10\bar{1}3)$ orientation is predominant, as evidenced by XRD.

Figure 5 shows AFM images ($3 \times 3 \mu\text{m}^2$) of the surface of the samples corresponding to the XRD and TEM results in Figs. 1 and 3. The observed surface morphology is consistent with the two types of orientations observed in XRD and TEM, i.e. basal-plane-oriented grains and a set of nonbasal-plane-oriented grains [known from XRD and TEM to have $(10\bar{1}3)$ planes parallel to the surface]. Especially the nonbasal grains either present six different orientations separated by $\sim 60^\circ$, highlighted by arrows in Fig. 5, or they form triangular structures when they meet, indicated by triangles. Therefore, the surface morphology shown by AFM images confirms the sixfold contribution of epitaxially oriented $(10\bar{1}3)$ grains as determined by pole figures (not shown). Typical grain sizes of the nonbasal grains are $\sim 200 \times 50 \text{ nm}^2$. This growth mode yields pits in the surface [see Figs. 5 and 5(c)] up to 50 nm in

FIG. 4. High-resolution TEM micrographs of phase-pure Cr_2GeC grown at a substrate temperature of 800°C (cf. Fig. 1). In (b), the (000ℓ) basal planes of Cr_2GeC are highlighted.

depth, determined by quantitative analysis of the AFM data. A close examination of the profile in depth also reveals a mosaic surface that may be responsible for the relatively large FWHM of the XRD rocking curves performed on Cr_2GeC 000ℓ peaks.

B. Effect of deposition temperature

Figure 6 shows x-ray diffractograms of Cr-Ge-C films deposited with the optimized composition (for growth of phase-pure Cr_2GeC at 800°C , cf. Sec. III A) at substrate temperatures in the range of 500 – 800°C . For the lowest temperatures (below 650°C), the peak at 35.34° can be identified as Cr_2GeC $10\bar{1}0$. The possibility that it could be related to Cr_3C_2 (which would also match this peak position) can be excluded since no other peaks from that phase are observed. The peak at 27.2° is Ge 111 and indicates surface segregation of Ge islands at lower temperatures (c.f. SEM results below). ERDA showed that all these films have essentially the same composition, $\text{Cr:Ge:C} = 0.52:0.24:0.24$ ($O < 0.001$) or $2:1:1$ within the uncertainty of the technique. The ERDA depth profiles were essentially identical for all these samples; a typical one is plotted in Fig. 7. As can be seen, the composition is constant throughout the whole depth of the film, except for surface oxides. Since the film thickness (~ 190 nm) is known from TEM, we can estimate the film density to be ~ 6.9 g/cm 3 from the ERDA

FIG. 5. (Color online) Topographic 3D top view AFM image recorded in tapping mode of a phase-pure Cr_2GeC sample shown in Figs. 1 and 3. The height profile corresponds to the white full line. Arrows indicate the main in-plane orientations of $(10\bar{1}3)$ grains.

profile. This is very close to the theoretical bulk density of Cr_2GeC , 6.88 g/cm 3 .¹

Close to the substrate/film interface in the depth profile in Fig. 7, one can get the impression that intermixing has occurred. This is actually not a diffusion profile but a measurement artifact due to the limited depth resolution of the ERDA measurement. Therefore, the apparent depth

FIG. 6. X-ray diffractograms of Cr-Ge-C films deposited with the optimized composition (for growth of phase-pure Cr_2GeC at 800°C , the same sample as in Fig. 1) at substrate temperatures in the range of 500 – 800°C .

FIG. 7. (Color online) Typical ERDA depth profile of Cr-Ge-C films deposited with optimized composition (for growth of phase-pure Cr_2GeC at 800°C). The ERDA depth profiles were essentially identical for films grown with this composition regardless of temperature (in the range of 500 – 800°C). The depth scale (top) is based on the film thickness of 190 nm determined by TEM.

profile corresponds to an actual depth profile with a sharp substrate/film interface, as demonstrated by high-resolution TEM.

Figure 8 shows SEM images of Cr_2GeC thin films deposited at substrate temperatures in the range of 500 – 800°C (i.e. the same films as in Fig. 6). Figures 8(a) and 8(b) show the films deposited at 800 and 700°C , respectively. They exhibit similar surface morphologies that are relatively smooth except for the growth pits also observed in AFM images (Fig. 5). The morphologies of the films grown at lower temperatures [600°C , Fig. 8(c), and 500°C , Fig. 8(d)] are different. Figure 8(c) shows a large number of Cr_2GeC grains with basal planes orthogonal to the surface, i.e. grains with $(10\bar{1}0)$ orientation (cf. the XRD results in Fig. 6) that yield a rough surface. Films grown at 500°C still comprise Cr_2GeC

FIG. 8. SEM images of Cr_2GeC thin films deposited at substrate temperatures of (a) 800°C , (b) 700°C , (c) 600°C , and (d) 500°C . Note: the scale in (d) differs from (a)–(c).

FIG. 9. θ - 2θ x-ray diffractograms of Cr-Ge-C films deposited at 800°C with varied Ge content.

with $(10\bar{1}0)$ and $(10\bar{1}3)$ orientation; however, in addition, Ge clusters several hundred nanometers in diameter have segregated on the surface. Each Ge cluster is most likely composed of many smaller (111) -oriented Ge grains, given the width of the Ge 111 peaks observed in XRD.

C. Variation of composition; role of competing phases

Figure 9 shows x-ray diffractograms of Cr-Ge-C films deposited at 800°C with varied Ge content (Ge target power in the range of 30 – 70 W). At the highest Ge content, the only impurity observed in XRD is Ge. Surface SEM images [not shown, but similar to Fig. 8(d)] of this sample showed that Ge formed islands on top of the surface. At low Ge content (Ge target power 30 – 40 W), Cr_2GeC is retained; however, the films are not phase pure but contain Cr_{23}C_6 . For the latter films, the Cr_2GeC is fully (000ℓ) -oriented, in contrast to the phase-pure films on the same substrate. For the lowest Ge content, the film contains a large amount of Cr_{23}C_6 , but for the film deposited with 40 W Ge target power, Cr_2GeC is the predominant phase.

Figure 10 shows x-ray diffractograms of Cr-Ge-C films deposited at 800°C with varied C content. The Ge power was 60 W , i.e. slightly higher than for the phase-pure films in Figs. 1 and 2. Hence, the nearly phase-pure film (second from top in Fig. 10, C target power of 260 W) contains a small fraction of Ge in addition to Cr_2GeC . A reduction in C content results in increased amounts of the C-poor impurity phases (Cr_{23}C_6 and $\text{Cr}_5\text{Ge}_3\text{C}_x$) as well as substantial amounts of pure Ge. Note that the Ge 200 peak at 45.3° and the Cr_2GeC peak at 44.9° are difficult to distinguish, but the Ge 111 peak at 27.3° is unambiguous. At the lowest C content (target power of 120 W , bottom of Fig. 10), $\text{Cr}_5\text{Ge}_3\text{C}_x$ is the dominant phase with some amount of Cr_2GeC and Cr_{23}C_6 . Increasing the C content (290 W , top of Fig. 10) relative to the nearly phase-pure Cr_2GeC (260 W) results in a reduction of the Cr_2GeC peak intensities and a strong increase in the Ge 111 peak.

D. Electrical properties

Four-point-probe room-temperature resistivity measurements were performed on selected Cr_2GeC samples: two thin

FIG. 10. θ - 2θ x-ray diffractograms of Cr-Ge-C films deposited at 800 °C with varied C content.

films on Al_2O_3 substrate [(10 $\bar{1}$ 3) and (000 ℓ) orientations, cf. Sec. III A] and the one with the TiN seed layer. A film thickness of 190 nm is assumed for all measured resistivities. This thickness determination is the main source of uncertainty in the numbers; i.e. the uncertainty (see below) is very small (a few percent) for the smooth (000 ℓ)-oriented films but considerably larger for the rougher (10 $\bar{1}$ 3)-oriented film. The measured resistivities are 66 $\mu\Omega\text{cm}$ for the (10 $\bar{1}$ 3)-oriented film and 53 $\mu\Omega\text{cm}$ for the (000 ℓ)-oriented film. The value obtained for the epitaxial (000 ℓ)-oriented film grown on the TiN seed layer is 55 $\mu\Omega\text{cm}$; this value, however, includes the contribution from the seed layer. A value of 66 $\mu\Omega\text{cm}$ was obtained for a sample with Ge excess (cf. Fig. 9). This sample apparently has similar crystalline quality and phase purity apart from the surface Ge islands that, as expected, do not contribute to the measured resistivity. In contrast, a sample with higher C content (cf. Fig. 10, top) yielded a measured room-temperature resistivity of 86 $\mu\Omega\text{cm}$, i.e. around 30% higher.

FIG. 11. Resistivity as a function of temperature for Cr_2GeC thin films mainly oriented (10 $\bar{1}$ 3) and (000 ℓ) (corresponding to the XRD patterns in Figs. 1 and 9, second from bottom, respectively).

Figure 11 shows temperature-dependent resistivity measurements in the temperature range of 15–295 K for the two Cr_2GeC thin films deposited on Al_2O_3 . The residual resistivity ratios [$\text{RRR} = \rho(295 \text{ K})/\rho(15 \text{ K})$] obtained from these curves are 10.4 and 9.9 for (10 $\bar{1}$ 3)– and (000 ℓ)-oriented samples, respectively. The values for room-temperature resistivity obtained from these curves are in good agreement with those obtained from the four-point-probe measurements: $\rho_{10\bar{1}3} = 58 \mu\Omega\text{cm}$ and $\rho_{0001} = 51 \mu\Omega\text{cm}$ (compared to 66 and 53 $\mu\Omega\text{cm}$). The difference between the $\rho_{10\bar{1}3}$ obtained from each method is a consequence of the measurement uncertainty and thus more pronounced for the (10 $\bar{1}$ 3)-oriented film, which is rougher than the (000 ℓ)-oriented films.

IV. DISCUSSION

A. Nucleation and growth

Our results show that phase-pure Cr_2GeC thin films can be grown by magnetron sputter deposition at 800 °C. For films grown directly onto Al_2O_3 (0001), there is a component of epitaxial basal-plane oriented Cr_2GeC ; however, the Cr_2GeC secondary grain population with (10 $\bar{1}$ 3) orientation is predominant. Several effects may contribute to explain these observations. First, it is likely that the basal plane growth (step-flow mode) does not result in full surface coverage because of limited adatom mobility at 800 °C. Therefore, nucleation of nonbasal-oriented grains can occur and, because of their faster growth rate, can become dominant. This has been observed previously for Ti_2AlN .⁴⁴ It is also consistent with the observation that a reduction in Ge content (Fig. 9) yields (000 ℓ)-oriented Cr_2GeC films containing Cr_{23}C_6 , since at these Ge-poor conditions the secondary nucleation of Cr_{23}C_6 grains would be expected to occur preferentially instead of nonbasal Cr_2GeC grains. However, this alone cannot explain why the occurrence of Cr_2GeC (10 $\bar{1}$ 3) is nearly negligible for growth onto TiN(111) and MgO(111). The diffusion rates (adatom mobilities) may differ on different growth surfaces, which may facilitate basal-plane growth on TiN(111) and MgO(111). A further possible effect stems from the lattice mismatch of $\sim 9\%$ between Cr_2GeC and Al_2O_3 (0001). Given this large lattice mismatch, strained heteroepitaxy is most unlikely to be the growth mode; rather, the heteroepitaxial growth is most likely relaxed by the introduction of misfit dislocations that can act as nucleation sites for the (10 $\bar{1}$ 3)-oriented grains and/or slow down surface diffusion of adatoms. This explanation would therefore be consistent with the observation that the use of a TiN(111) seed layer or an MgO(111) substrate, which are better lattice matched, yields nearly global epitaxial growth. Finally, it should be stressed that additional epitaxial relations between Al_2O_3 and MAX phases exist^{37,45,46} and correspond to nonbasal epitaxial alignment, which could also trigger nucleation of (10 $\bar{1}$ 3) grains.

B. Temperature dependence

Our results show that Cr_2GeC can be grown down to 500 °C, and it may be possible to grow this phase at even lower substrate temperatures (which is possible for Cr_2AlC and V_2GeC). The films are, however, not epitaxial at this temperature. In contrast to the films deposited at 700–800 °C, the ones grown

at 500–600 °C are polycrystalline with (10 $\bar{1}$ 0)-dominated orientation; i.e. with a dominant contribution from standing basal planes (orthogonal to the substrate surface). Also, SEM and XRD show Ge surface segregation at these temperatures. These observations can be explained as a consequence of the fast growth and Ge-diffusion rates along the basal planes. The phenomenon of surface Ge segregation is similar to what has been observed for Ti₂GeC by Emmerlich *et al.*²⁶; the effect is even more pronounced for Sn, a larger group-14 element than Ge, as observed²⁶ for Ti₂SnC. In contrast, the Ti-Si-C based MAX phases appear less sensitive; here, Si will typically float on top of the growing film during the initial stages of growth, but once sufficient supersaturation has been achieved, Ti₃SiC₂ (or Ti₄SiC₃) nucleates rather than segregating Si.^{2,17,47}

C. Electrical properties

The room-temperature resistivity of our samples is 53–66 $\mu\Omega\text{cm}$. There are no reliable reports on the conductivity of bulk Cr₂GeC, but our values are slightly lower than those reported for bulk Cr₂AlC (72–74 $\mu\Omega\text{cm}$).^{48,49} We consider our numbers quite robust as they are repeatable for numerous samples and in the expected range. The Cr-containing MAX carbides are expected to be among the ones with highest resistivity. For example, it is known that² Cr₂AlC has much lower conductivity than Ti₂AlC (group 4 M element) and V₂AlC (group 5 M element). The reason is that in Cr₂AlC (group 6 M element), the hybridized Cr *d*-Al *p* states are primarily filled,⁵⁰ leading to relatively low conductivity because of reduced mobility.⁴⁸ The same argument is most likely valid for the series Ti₂GeC-V₂GeC-Cr₂GeC; the reported resistivities of the former two are in the range of 15–30 $\mu\Omega\text{cm}$ compared to 53–67 $\mu\Omega\text{cm}$ for the present Cr₂GeC films. Furthermore, the RRR values of ~ 10 indicate high crystalline quality (in this context).

With resistivity data on samples of both predominant (10 $\bar{1}$ 3) and (000 ℓ)-oriented films, we can discuss the anisotropy in the conductivity of Cr₂GeC and other MAX phases. From a naïve point of view, the conductivity anisotropy of Cr₂GeC would be related to its anisotropic electronic structure. Figure 12 shows the calculated band structure of Cr₂GeC. For the $\Gamma \rightarrow A$, $H \rightarrow K$, and $M \rightarrow L$ directions, which are related to the *c*-axis electronic response, only one band crosses the Fermi level (in the $M \rightarrow L$ direction). This is different from the other orientations, where several bands cross the Fermi energy within the $\Gamma \rightarrow K$, $\Gamma \rightarrow L$, $A \rightarrow H$, and $L \rightarrow H$ directions, which correspond to the basal plane response. However, this simple argument does not accurately describe the transport properties of MAX phases. It is by now well established (see Ref. 2 for a review) that MAX phase transport properties cannot be understood only from ground state electronic structure calculations, i.e. band velocity or the density of states at the Fermi level [$\text{DOS}(E_F)$], but are largely determined by scattering processes. The carrier mobilities are actually much lower in the Cr-containing MAX phases than in the Ti-based ones, which is not surprising since the main contribution to conduction in MAX phases is from M *d* states (i.e. the electronic states around the Fermi level). Strongly localized *d* states are not expected to have high mobilities. For bulk MAX phases, it is often assumed that the mobility

FIG. 12. (Color online) Band structure (the Fermi level is indicated by a horizontal full line) and first Brillouin zone of Cr₂GeC.

is proportional to the inverse of $\text{DOS}(E_F)$, consistent with the trends for the resistivities of the series Ti₂GeC-V₂GeC-Cr₂GeC and Ti₂AlC-V₂AlC-Cr₂AlC (see above). However, this assumption (the Mott approximation for transition metals) means that scattering is isotropic; it is therefore only valid for polycrystalline samples and cannot explain anisotropy effects.

There are several reports discussing resistivity anisotropy in MAX phases by comparing measured values for bulk and for oriented thin films. However, some of these do not investigate phase-pure samples,^{51,52} and in those cases, any differences observed between bulk resistivity and measured resistivities for thin films can be explained by large amounts of secondary phases rather than by anisotropy. Scabarozzi *et al.*²⁵ performed measurements on phase-pure, high-quality epitaxial (000 ℓ)-oriented Ti₂GeC, and a comparison with bulk polycrystalline samples suggested that the anisotropy in the conductivity is relatively weak (a factor of 1.6 between *c*-axis conductivity and in-plane conductivity).

To relate these to the present results, it should first be mentioned that the resistivity of the (10 $\bar{1}$ 3)-oriented film is a mix between the basal plane and *c*-axis response. Nevertheless, some conclusions can be drawn about anisotropy by comparing the ideal resistivities of the two samples in Fig. 11. The ideal resistivity is obtained from Matthiessen's law:

$$\rho(T) = \rho_r + \rho_i(T), \quad (1)$$

where T is temperature, ρ the total resistivity, ρ_r the residual resistivity, and ρ_i the ideal resistivity. Here ρ_i depends only on the charge carrier-phonon coupling (i.e. it does not depend on defect and impurity densities). As ρ_i varies linearly with temperature in the range of 100–300 K, we can calculate the slope of the linear variation, which thus gives information on the charge carrier-phonon coupling. The slopes are 0.21 and 0.18 $\mu\Omega\text{cm}/\text{K}$ for the (10 $\bar{1}$ 3)– and (000 ℓ)-oriented samples, respectively. These values evidence a relatively strong charge carrier-phonon coupling in MAX phase materials. For comparison, slopes are about 6.10 $\times 10^{-3}$ $\mu\Omega\text{cm}/\text{K}$ for Cu or 5 $\mu\Omega\text{cm}/\text{K}$ for YBa₂Cu₃O₇, where electron-phonon coupling is, respectively, weak and strong.⁵³ Since the electron-phonon coupling is expected to be strong in the Cr-containing MAX phases,¹⁴ this is not surprising. These results differ from measurements carried on a bulk Ti₂GeC sample and a (000 ℓ)-oriented Ti₂GeC epitaxial thin film (cf. Fig. 1 in Ref. 25) in that the slopes of the resistivity curves are about a factor of two larger for the present Cr₂GeC films than for Ti₂GeC. This is consistent with the expectation that the electron-phonon coupling is expected to be much more important in Cr₂GeC than in Ti₂GeC.¹⁴ Moreover, the charge carrier-phonon coupling is likely anisotropic, as indicated by the differences in the slopes of the resistivity curves between films of different orientation. The magnitude of the anisotropy is similar to that of typical hexagonal close-packed metals.⁵⁴ This is in contrast to the much larger anisotropy one would expect from the naïve picture, based on inspection of the band structure. Based on these results, we can therefore argue that the difference in intrinsic resistivity of thin films with different orientations is not primarily an effect of the anisotropic band structure of Cr₂GeC but rather reflects anisotropy of the electron-phonon coupling. Such anisotropy of the charge carrier-phonon coupling further underscores the limitations of interpreting MAX phases transport properties in terms of ground state electronic structure calculations. This reasoning is further supported by determination of anisotropies in dielectric responses, carrier lifetimes, and scattering process of Ti₂AlN, Ti₂AlC, Ti₃AlC₂, and Ti₃SiC₂.^{55–57}

V. CONCLUSIONS

For films deposited directly onto Al₂O₃(0001), phase-pure Cr₂GeC can be grown at temperatures above 700–800 °C. These films have an epitaxial component with the well-known epitaxial relationship Cr₂GeC(0001)//Al₂O₃(0001) and Cr₂GeC(11 $\bar{2}$ 0)//Al₂O₃(1 $\bar{1}$ 00) or Cr₂GeC(11 $\bar{2}$ 0)//Al₂O₃($\bar{1}$ 2 $\bar{1}$ 0). There is also a secondary grain population with (10 $\bar{1}$ 3) orientation. In contrast, deposition onto Al₂O₃(0001) with TiN(111) seed layer and MgO(111) yielded growth of globally epitaxial Cr₂GeC(0001) with a virtually negligible (10 $\bar{1}$ 3) contribution. Possible explanations for this are that the adatom mobilities may differ on different growth surfaces, which may facilitate basal-plane growth on TiN(111) and MgO(111), and that the large lattice mismatch causes the introduction of misfit dislocations that may act as nucleation sites for secondary grain populations. In contrast to the films deposited at 700–800 °C, the ones grown at 500–600 °C are polycrystalline Cr₂GeC with predominant (10 $\bar{1}$ 0) orientation; they also exhibit surface segregations of Ge as a consequence of the fast Ge-diffusion rates along the basal planes. The room-temperature resistivity of our samples is between 53 and 66 $\mu\Omega\text{cm}$. Temperature-dependent resistivity measurements show that the charge carrier-phonon coupling is substantial and likely anisotropic and emphasizes the limitations of interpreting MAX phases transport properties only in terms of ground state electronic structure calculations.

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¹M. W. Barsoum, *Prog. Solid State Chem.* **28**, 201 (2000).

²P. Eklund, M. Beckers, U. Jansson, H. Högborg, and L. Hultman, *Thin Solid Films* **518**, 1851 (2010).

³J. Y. Wang and Y. C. Zhou, *Annu. Rev. Mater. Res.* **39**, 415 (2009).

⁴W. Jeitschko, H. Nowotny, and F. Benesovsky, *Monatsh. Chem.* **94**, 844 (1963).

⁵S. Amini, A. Zhou, S. Gupta, A. DeVillier, P. Finkel, and M. W. Barsoum, *J. Mater. Res.* **23**, 2157 (2008).

⁶T. H. Scabarozi, S. Amini, O. Leaffer, A. Ganguly, S. Gupta, W. Tambussi, S. Clipper, J. E. Spanier, M. W. Barsoum, J. D. Hettinger, and S. E. Lofland, *J. Appl. Phys.* **105**, 013543 (2009).

⁷N. J. Lane, S. C. Vogel, and M. W. Barsoum, *J. Amer. Ceram. Soc.* to be published (2011), doi: 10.1111/j.1551-2916.2011.04609.x.

⁸B. Manoun, S. Amini, S. Gupta, S. K. Saxena, and M. W. Barsoum, *J. Phys. Condens. Matter* **19**, 456218 (2007).

⁹N. A. Phatak, S. R. Kulkarni, V. Drozd, S. K. Saxena, L. W. Deng, Y. W. Fei, J. Z. Hu, W. Luo, and R. Ahuja, *J. Alloys Compd.* **463**, 220 (2008).

¹⁰D. Jürgens, M. Uhrmacher, H. Hofsäss, J. Mestnik-Filho, and M. W. Barsoum, *Nucl. Instrum. Methods Phys. Res., Sect. B* **268**, 2185 (2010).

¹¹A. Bouhemadou, *Appl. Phys. A* **96**, 959 (2009).

¹²W. Zhou, L. J. Liu, and P. Wu, *J. Appl. Phys.* **106**, 033501 (2009).

¹³M. K. Drulis, H. Drulis, A. E. Hackemer, O. Leaffer, J. Spanier, S. Amini, M. W. Barsoum, T. Guilbert, and T. El-Raghy, *J. Appl. Phys.* **104**, 023526 (2008).

¹⁴S. E. Lofland, J. D. Hettinger, T. Meehan, A. Bryan, P. Finkel, S. Gupta, M. W. Barsoum, and G. Hug, *Phys. Rev. B* **74**, 174501 (2006).

¹⁵S. E. Lofland, J. D. Hettinger, K. Harrell, P. Finkel, S. Gupta, M. W. Barsoum, and G. Hug, *Appl. Phys. Lett.* **84**, 508 (2003).

¹⁶M. K. Drulis, H. Drulis, S. Gupta, M. W. Barsoum, and T. El-Raghy, *J. Appl. Phys.* **99**, 093502 (2006).

- ¹⁷J. Emmerlich, H. Högberg, S. Sasvari, P. O. Å. Persson, L. Hultman, J. P. Palmquist, U. Jansson, J. M. Molina-Aldareguia, and Z. Czigany, *J. Appl. Phys.* **96**, 4817 (2004).
- ¹⁸M. Magnuson, J. P. Palmquist, M. Mattesini, S. Li, R. Ahuja, O. Eriksson, J. Emmerlich, O. Wilhelmsson, P. Eklund, H. Högberg, L. Hultman, and U. Jansson, *Phys. Rev. B* **72**, 245101 (2005).
- ¹⁹P. Eklund, C. Virojanadara, J. Emmerlich, L. I. Johansson, H. Högberg, and L. Hultman, *Phys. Rev. B* **74**, 045417 (2006).
- ²⁰K. Buchholt, P. Eklund, J. Jensen, J. Lu, A. Lloyd Spetz, and L. Hultman, *Scr. Mater.* **64**, 1141 (2011).
- ²¹K. Buchholt, R. Ghandi, M. Domeij, C. M. Zetterling, J. Lu, P. Eklund, L. Hultman, and A. Lloyd Spetz, *Appl. Phys. Lett.* **98**, 042108 (2011).
- ²²Z. C. Wang, S. Tsukimoto, R. Sun, M. Saito, and Y. Ikuhara, *Appl. Phys. Lett.* **98**, 104101 (2011).
- ²³H. Högberg, P. Eklund, J. Emmerlich, J. Birch, and L. Hultman, *J. Mater. Res.* **20**, 779 (2005).
- ²⁴H. Högberg, L. Hultman, J. Emmerlich, T. Joelsson, P. Eklund, J. M. Molina-Aldareguia, J. P. Palmquist, O. Wilhelmsson, and U. Jansson, *Surf. Coat. Technol.* **193**, 6 (2005).
- ²⁵T. H. Scabarozi, P. Eklund, J. Emmerlich, H. Högberg, T. Meehan, P. Finkel, M. W. Barsoum, J. D. Hettinger, L. Hultman, and S. E. Lofland, *Solid State Commun.* **146**, 498 (2008).
- ²⁶J. Emmerlich, P. Eklund, D. Rittrich, H. Högberg, and L. Hultman, *J. Mater. Res.* **22**, 2279 (2007).
- ²⁷O. Wilhelmsson, P. Eklund, H. Högberg, L. Hultman, and U. Jansson, *Acta Mater.* **56**, 2563 (2008).
- ²⁸M. Magnuson, O. Wilhelmsson, M. Mattesini, S. Li, R. Ahuja, O. Eriksson, H. Högberg, L. Hultman, and U. Jansson, *Phys. Rev. B* **78**, 035117 (2008).
- ²⁹R. Mertens, Z. M. Sun, D. Music, and J. M. Schneider, *Adv. Eng. Mater.* **6**, 903 (2004).
- ³⁰C. Walter, D. P. Sigumonrong, T. El-Raghy, and J. M. Schneider, *Thin Solid Films* **515**, 389 (2006).
- ³¹J. M. Schneider, D. P. Sigumonrong, D. Music, C. Walter, J. Emmerlich, R. Iskandar, and J. Mayer, *Scr. Mater.* **57**, 1137 (2007).
- ³²Q. M. Wang, A. Flores Renteria, O. Schroeter, R. Mykhalonka, C. Leyens, W. Garkas, and M. to Baben, *Surf. Coat. Technol.* **204**, 2343 (2010).
- ³³J. J. Li, L. F. Hu, F. Z. Li, M. S. Li, and Y. C. Zhou, *Surf. Coat. Technol.* **204**, 3838 (2010).
- ³⁴Q. M. Wang, R. Mykhalonka, A. Flores Renteria, J. L. Zhang, C. Leyens, and K. H. Kim, *Corrosion Science* **52**, 3793 (2010).
- ³⁵T. H. Scabarozi, Ph.D. thesis (Drexel University, Philadelphia, 2009), available online through [<http://idea.library.drexel.edu/>].
- ³⁶G. Abadias, L. E. Koutsokeras, Ph. Guerin, and P. Patsalas, *Thin Solid Films* **518**, 1532 (2009).
- ³⁷J. Frodelius, P. Eklund, M. Beckers, P. O. Å. Persson, H. Högberg, and L. Hultman, *Thin Solid Films* **518**, 1621 (2010).
- ³⁸H. J. Whitlow, G. Possnert, and C. S. Petersson, *Nucl. Instrum. Methods Phys. Res., Sect. B* **27**, 448 (1987).
- ³⁹M. S. Janson, *CONTES, Conversion of Time-Energy Spectra, A Program for ERDA Data Analysis* (unpublished manual, Uppsala University, 2004).
- ⁴⁰I. Horcas, R. Fernandez, J. M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero, and A. M. Baro, *Rev. Sci. Instrum.* **78**, 013705 (2007).
- ⁴¹P. Blaha, K. Schwarz, G. H. K. Madsen, D. Kvaniscka, and J. Luitz, *WIEN2k, An Augmented PLane Wave+Local Orbitals Program for Calculating Crystal Properties* (Technische Universität Wien, Austria, 2001).
- ⁴²Z. J. Lin, M. S. Li, and Y. C. Zhou, *J. Mater. Sci. Technol.* **23**, 145 (2007).
- ⁴³P. Eklund, A. Murugaiah, J. Emmerlich, Z. Czigany, J. Frodelius, M. W. Barsoum, H. Högberg, and L. Hultman, *J. Cryst. Growth* **304**, 264 (2007).
- ⁴⁴M. Beckers, C. Höglund, C. Baehtz, R. M. S. Martins, P. O. Å. Persson, L. Hultman, and W. Möller, *J. Appl. Phys.* **106**, 064915 (2009).
- ⁴⁵D. P. Sigumonrong, J. Zhang, Y. C. Zhou, D. Music, J. Emmerlich, J. Mayer, and J. M. Schneider, *Scr. Mater.* **64**, 347 (2011).
- ⁴⁶M. D. Tucker, P. O. Å. Persson, M. C. Guenette, J. Rosén, M. M. Bilek, and D. R. McKenzie, *J. Appl. Phys.* **109**, 014903 (2011).
- ⁴⁷P. Eklund, M. Beckers, J. Frodelius, H. Högberg, and L. Hultman, *J. Vac. Sci. Technol. A* **25**, 1381 (2007).
- ⁴⁸J. D. Hettinger, S. E. Lofland, P. Finkel, T. Meehan, J. Palma, K. Harrell, S. Gupta, A. Ganguly, T. El-Raghy, and M. W. Barsoum, *Phys. Rev. B* **72**, 115120 (2005).
- ⁴⁹W. B. Tian, P. L. Wang, G. J. Zhang, Y. M. Kan, Y. X. Li, and D. S. Yan, *Scr. Mater.* **54**, 841 (2006).
- ⁵⁰Z. M. Sun, D. Music, R. Ahuja, and J. M. Schneider, *J. Phys. Condens. Matter* **17**, 7169 (2005).
- ⁵¹T. H. Scabarozi, J. Roche, A. Rosenfeld, S. H. Lim, L. Salamanca-Riba, G. Yong, I. Takeuchi, M. W. Barsoum, J. D. Hettinger, and S. E. Lofland, *Thin Solid Films* **517**, 2920 (2009).
- ⁵²M. C. Guenette, M. D. Tucker, M. Ionescu, M. M. M. Bilek, and D. R. McKenzie, *Thin Solid Films* **519**, 766 (2010).
- ⁵³M. Gerl and J. P. Issi, *Traité des Matériaux: Physique des Matériaux*, Presses Polytechniques et Universitaires Romandes (1997).
- ⁵⁴B. A. Sanborn, P. B. Allen, and D. A. Papaconstantopoulos, *Phys. Rev. B* **40**, 6037 (1989).
- ⁵⁵N. Haddad, E. Garcia-Laurel, L. Hultman, M. W. Barsoum, and G. Hug, *J. Appl. Phys.* **104**, 023531 (2008).
- ⁵⁶G. Hug, P. Eklund, and A. Orchowski, *Ultramicroscopy* **110**, 1054 (2010).
- ⁵⁷V. Mauchamp, G. Hug, M. Bugnet, T. Cabioc'h, and M. Jaouen, *Phys. Rev. B* **81**, 035109 (2010).