Room-Temperature Deintercalation and Self-Extrusion of Ga from Cr_2GaN

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Bulk samples of the layered ternary nitride Cr_2GaN were observed to extrude filaments of pure elemental gallium at room temperature. This self-extrusion phenomenon is best described as a room-temperature deintercalation of gallium from the basal planes of porous Cr_2GaN samples. The extruded filaments are single crystals with 2- to 100-micrometer diameters and can be several centimeters long.

Recently, two families of structurally related ternary nitrides and carbides, namely, the M_3BX_2, or 312 phases, and the M_2BX, or 211 phases, where M is an early transition metal, B is a B-group element, and X is C or N, were identified and shown to have an unusual combination of properties (*1–5*). Here, we report on a previously unobserved physical phenomenon—the self-extrusion of Ga whiskers—that we observed in porous bulk samples of Cr_2GaN. Like the other 211's, the structure of Cr_2GaN, consisting of Cr-N layers interleaved with layers of pure Ga, is hexagonal with lattice parameters *a* and *c* of 2.88 and 12.7 Å, respectively (*6*).

Coarse Ga shots (≈2 mm; GFI Advanced Technology, 99.99% purity) and CrN and Cr (−325 mesh; Alfa Johnson Matthey), both 99.8% pure, were weighed to correspond to the 211 chemistry, hand mixed, and cold pressed into pellets 32 mm by 12 mm by 12 mm; sealed in evacuated borosilicate glass tubes; and hot isostatically pressed at 850°C for 8 hours. Because 850°C is above the decomposition temperature of Cr_2GaN, upon cooling, the material consisted of CrN, $CrGa_4$, and Cr_3GaN. To convert the specimen to Cr_2GaN, we further annealed it for 24 hours at 740°C in an evacuated glass tube and air quenched it. X-ray diffraction (XRD) of the quenched samples (Fig. 1A) indicated that they were predominantly single-phase Cr_2GaN with minor amounts (≈5 vol %) of CrN. The microstructure consists of small equiaxed grains of 0.5- to 2-μm diameter. The samples were not fully dense but had some open interconnected pores with typical pore sizes in the 0.3- to 5-μm range.

After fabrication, the samples were lightly polished and exposed to the ambient environment for 24 to 48 hours, at which time filaments, visible to the naked eye, appeared on the surface. The absence of Ga XRD peaks before exposure and their appearance after exposure, concomitant with a decrease in the intensity of the (0006) peaks, are compelling evidence that the Ga source is the basal planes of Cr_2GaN. This decrease in intensity was confirmed by simulation of XRD spectra (*7*).

Scanning electron microscopy (SEM) micrographs of a typical surface that was lightly polished and exposed to air for ≈2 to 3 days show that the filaments appear to have been extruded from the bulk; energy-dispersive spectroscopy showed that they are made up of elemental Ga. Evidence that these filaments were forced to flow through a channel is multifold: (i) no two filaments have the same cross section or shape; (ii) channel marks, mostly striations, are visible on all of the filament surfaces; and (iii) the presence of helical shapes that can most easily be obtained by extrusion is seen. For example, the simplest explanation for the various shapes taken by the coiled filament (apparent in the near center of Fig. 2A and shown at a higher magnification in Fig. 2B), which originally emerged from the substrate at the lower left corner as a tight spiral and continued growing from its base, changing shape as it did, is that the shape of the orifice through which it was extruded was itself continually changing shape.

The formation and growth of the filaments only occur near the surface; Ga peaks were not observed in the XRD patterns of freshly fractured surfaces of samples that were exposed to the atmosphere. This finding was corroborated by SEM; cross sections of active surfaces indicated that the roots of the filaments were shallow and in the 2- to 20-μm range. In other words, these filaments grow in the same way hair grows, from the base. A Laue pattern of a ≈2-cm-long whisker indicated that it was a single crystal.

In the time frame of days, the growth of the filaments is far from uniform, which indicates that either a catalyst, microcracks, or some peculiar geometric arrangement of the pores is required. For the most part, exposure of the fractured surfaces to the atmosphere does not result in the immediate formation and growth of these filaments, but light polishing renders the inactive fractured surfaces active—the introduction of some surface damage by light polishing accelerates or catalyzes this phenomenon. Furthermore, the concentration of the filaments was found to be a function of sample density, with higher density samples showing less activity. Some fractured surfaces become active but only after prolonged exposure to the atmosphere. For example, exposure of a fractured surface to the atmosphere for about 6 months resulted in a marked increase in the density of the filaments, their lengths, and their thicknesses (Fig. 2D). It appears that after prolonged exposure, most, if not all, pores are active.

The absence of filaments much smaller than 2 μm eliminates surface energy as a driving force. Instead, we propose that the Ga is extruded from preexisting pores in the samples. The Poiseuille pressure (*P*) needed to drive Ga of viscosity η, through a channel of radius *r* and length *L*, is given by

$$\Delta P = \frac{8\eta L Q}{\pi r^4} \qquad (1)$$

where *Q* is the volumetric flow rate. Consider the filament shown in Fig. 2D, which grew to about 2 mm in about 50 hours. If the channel length (that is, the root of the filament) is conservatively assumed to be 50 μm and the viscosity of Ga at room temperature, which is

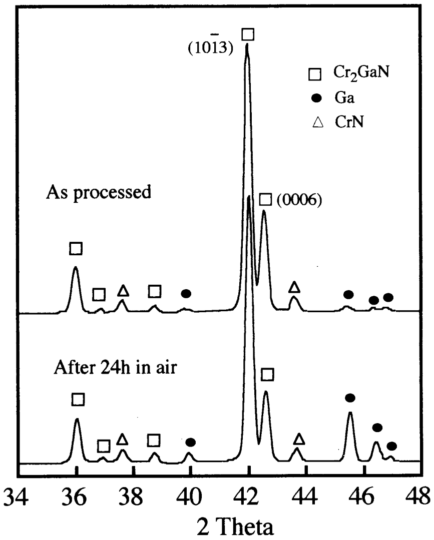

Fig. 1. XRD of as-processed samples of Cr_2GaN and the same surface after exposure to the atmosphere for 24 hours at room temperature. Note emergence of Ga peaks and reduction in the peak intensities of the basal, or (0006), planes of Cr_2GaN.

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>0.98 of its melting point, is on the order of 10^5 Pa·s, the pressure drop across the channel length is on the order of 17 kPa. The highest uncertainty in the aforementioned calculations is in the value of η; even if $\eta = 10^8$ Pa·s, that translates to a pressure drop of 17 MPa. It is unlikely that the filaments at 0.98 of their melting point would have a viscosity greater than 10^8 Pa·s. As discussed below, such modest stresses can easily be generated if the volume changes for the reactions suggested below are assumed to be positive. The volumetric strain required to produce a stress, σ, is given by

$$\frac{\Delta V}{V_0} = \frac{3(1 - 2\nu)}{E}\sigma \qquad (2)$$

where E and ν are Young's modulus and Poisson's ratio, respectively, of Cr_2GaN. If we assume that E and ν are 150 GPa and 0.2 (*8*), respectively, the volumetric strain needed to generate a pressure of ≈20 MPa is 2.4×10^{-4}, which is a very modest strain indeed.

There are two plausible driving forces for this process. The first is that the solubility of Ga in Cr_2GaN at room temperature is less than that at the processing temperature and what is observed is simply the rejection of excess Ga. In other words, the following reaction is occurring:

$$Cr_2GaN = Cr_2Ga_{1-y}N + yGa(s) \qquad (3)$$

An alternative, and more likely, explanation is that the following reaction is occurring:

$$Cr_2GaN + y/xX_x = Cr_2(X_yGa_{1-y})N + yGa(s) \qquad (4)$$

where X_x is a gas in the atmosphere, possibly O_2 or N_2. At this time, we cannot rule other reactive gases such as H_2O or CO_2. In reaction 4, X_x is assumed to replace the Ga in the basal planes. The overall volume changes for these reactions are unknown but are almost certainly positive because Ga is one of the few elements that expand on solidification. For example, the volume change for the decomposition of Cr_2GaN into solid Ga and Cr_2N is +13 vol %, which corresponds to roughly 500 times the strain needed for the extrusion. It thus follows that the driving force for the extrusion is most likely the positive volume change of either reaction 3 or 4.

The hemispherical radius of the volume of Cr_2GaN required, assuming it converts completely to Cr_2N (that is, reaction 3 is operative), to produce the 2-mm-long filament shown in Fig. 2C is on the order of 20 μm. If the assumption is that only 10% of the available Ga atoms are rejected or replaced, the distance increases to ≈30 μm. Thus, roughly 30,000 grains must simultaneously pool their Ga to produce the filament shown in Fig. 2C. At this time, the diffusion path of the Ga to the surface is unknown, but given that some surface damage appears to catalyze the phenomenon, it is not unreasonable to assume that Ga diffuses along microcracks introduced by the damage.

The implications and potential applications of this phenomenon in general, and Cr_2GaN in particular, are numerous and consequential. If reaction 4 is operative and reversible, then changes of some physical property, such as conductivity or surface reflectivity, can be correlated with the partial pressure of the reactant gas, in which case Cr_2GaN could be used as a sensor. Furthermore, when the driving forces and extrusion mechanisms are better understood, it is conceivable that the shape and form of the filaments can be manipulated and controlled and hence exploited to fabricate micrometer-sized wires, springs, and rods. With Micro Electro-Mechanical Systems technology and the continual shrinking of parts and components, smaller and smaller wires will be required. The phenomenon described in this report is potentially a viable technique to fabricate single crystals of such wires, which would have the added advantage of being mechanically robust, the extent of which is clear in Fig. 2, in which the complex shapes are maintained despite the whiskers being at 0.98 of their melting point. Needless to say, Ga, with its low melting point, would be of limited use. However, Si and Ge are two other elements that expand on solidification, and if this phenomenon can be reproduced at higher temperatures, in say Ti_3SiC_2 or Ti_3GeC_2, or possibly Ti_2AlC, then Si, Ge, and Al micrometer-sized whiskers, or other shapes, could in principle, be produced.

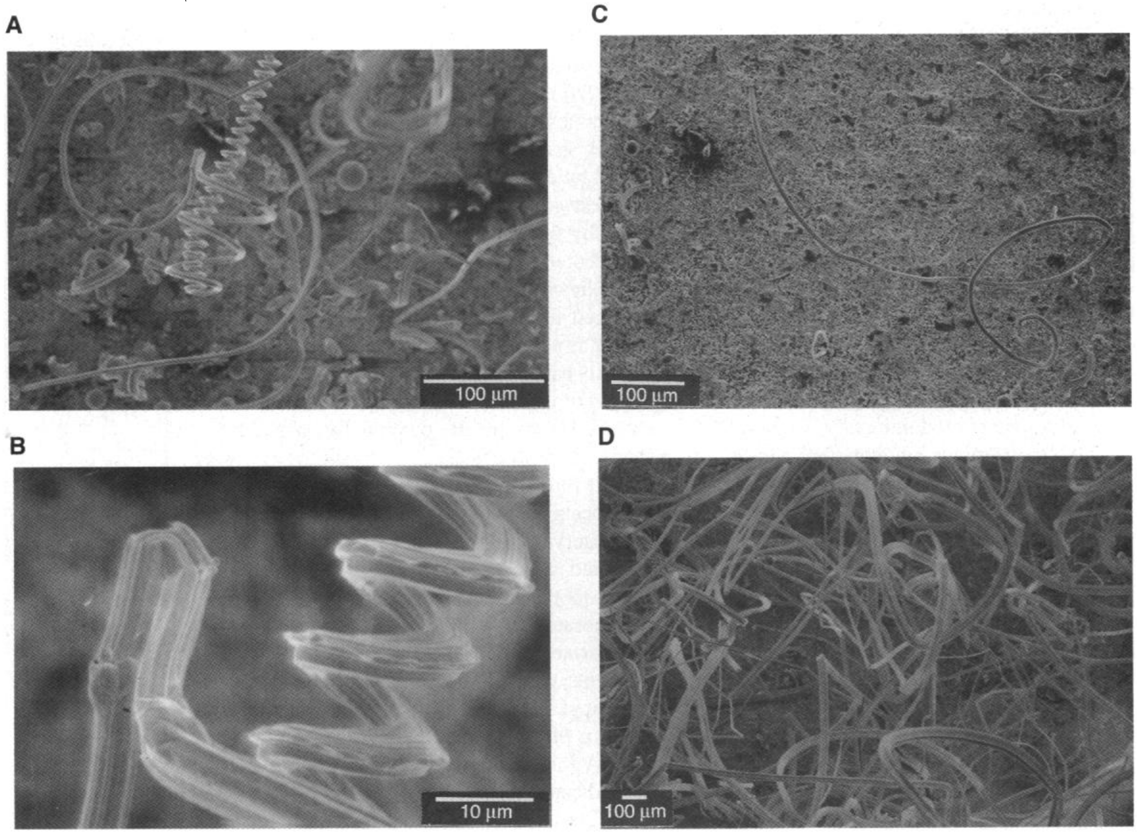

Fig. 2. A series of SEM images of the surface of a Cr_2GaN sample exposed to the atmosphere for 50 hours (**A**). Filaments observed are pure single crystalline Ga. (**B**) Same as (A), but at higher magnification. (**C**) Same as (A), but at a different location. (**D**) The sample after six months, showing marked increase in density and lengths of whiskers.

If microcracks indeed catalyze the reaction, then lasers, among other techniques, could be used to scribe fine patterns and microcircuits on the surface that would be preferentially filled with the B-group element. If scratched above the melting point of Ga, scratches immediately fill up with molten Ga. Once patterned, the B-group elements could then be doped to form semiconductor-based devices. For example, Ga could be nitrided to form GaN and hence GaN-based devices. Finally, the results of this work further reinforce the notion that the B-group element is relatively weakly bound in the structure (*3–5*) and hence easily chemically displaceable. Consequently, it is not unreasonable to assume that this replacement-displacement reaction could also be carried out electrochemically. It is thus anticipated that a majority, if not all, of the 312's and 211's could potentially be useful intercalation compounds.

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9. We thank T. Twardowski and A. Zavaliangos for stimulating discussions and T. El-Raghy for carrying out some experiments and for many very fruitful discussions. The help of M. Gamarnik in carrying out the Laue experiments is appreciated.

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Mercury in a Spanish Peat Bog: Archive of Climate Change and Atmospheric Metal Deposition

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A peat core from a bog in northwest Spain provides a record of the net accumulation of atmospheric mercury since 4000 radiocarbon years before the present. It was found that cold climates promoted an enhanced accumulation and the preservation of mercury with low thermal stability, and warm climates were characterized by a lower accumulation and the predominance of mercury with moderate to high thermal stability. This record can be separated into natural and anthropogenic components. The substantial anthropogenic mercury component began ~2500 radiocarbon years before the present, which is near the time of the onset of mercury mining in Spain. Anthropogenic mercury has dominated the deposition record since the Islamic period (8th to 11th centuries A.D.). The results shown here have implications for the global mercury cycle and also imply that the thermal lability of the accumulated mercury can be used not only to quantify the effects of human activity, but also as a new tool for quantitative paleotemperature reconstruction.

Mercury is an important trace metal in the environment because of its complex behavior and the high potential toxicity of its methylated species. Gaseous elemental Hg has a long atmospheric residence time (1 year), which favors long-range transport and homogenization on a hemispherical scale. Global mercury emissions have increased substantially at least during the past 100 to 150 years, and they have accumulated in various ecosystems (*1*). Although local decreases have been seen in some locations (mainly because of the reduction of emissions of regional sources), in general, Hg burdens have not declined. These observations suggest that atmospheric Hg emissions are complicated and that it can be difficult to separate natural and anthropogenic Hg emissions (*1, 2*). Evaluating the impact of anthropogenic emissions requires a knowledge of the natural background values and cycling processes (*2*). As a liquid at room temperature (melting point, 234.28 K) with a low enthalpy of vaporization ($\Delta H_{\mathrm{vap}} = 59.15$ kJ/mol), physical transformations of Hg (such as volatilization, condensation, and so forth) may have been important in pre-anthropogenic times because of the dramatic climate (especially temperature) changes that characterize the Holocene (*3*).

Here, we present a record of Hg deposition in the peat bog of Penido Vello (PVO), which extends to 4000 radiocarbon years before the present (^{14}C yr B.P.). Cadmium, Zn, and Pb were previously analyzed (*4*) in a core from this bog, which is situated in Galicia, northwest Spain (43°32′N, 7°34′W). This site is 600 km northwest of Almadén, the site of the largest Hg mine in the world. Mining activity here extends to Roman times and perhaps even earlier. In addition, the bog is ombrotrophic (*4*), meaning that elements such as Hg were supplied to the peat exclusively by atmospheric deposition.

A core of 2.5 m was sampled at intervals of 2 cm in the upper 1 m and at intervals of 5 cm below that depth. Total Hg concentrations were measured in wet samples ($\mathrm{Hg_T}$) and in samples that were dried for 2 weeks at 30°C (Hg_{30°) and 105°C (Hg_{105°) (*5*).

The lowest $\mathrm{Hg_T}$ concentrations of the PVO core is 22 ng g^{-1} at 170 to 175 cm, and the maximum is 436 ng g^{-1} in the uppermost peat sample. These values exceed the concentration in bedrock (1.52 ng g^{-1}) by 14 to 290 times and imply that the rock was not an important source of Hg to the overlying layers. High Hg concentrations are found at the surface and at depths of 17 cm (191 ng g^{-1}), 41 cm (65 ng g^{-1}), and 97 cm (45 ng g^{-1}) (Fig. 1, A and B). The concentrations in the deeper layers are far from constant (Fig. 1B). In general, there is an increase in $\mathrm{Hg_T}$ from 70 cm to the top of the core, but there are also higher values between 195 and 250 cm, followed by other local maxima (of ~40 to 45 ng g^{-1}). These deeper $\mathrm{Hg_T}$ peaks are not related to the ash content or bulk density of the peat, these properties being almost constant throughout the profile. They can only be partially explained by the history of mining and metallurgy in Almadén (*6*). The peak at 17 cm, dated between 600 and 200 years ago, cannot be fully explained by mining or metallurgy activities as there is no agreement between Hg production and the higher concentrations for those times and because the relatively higher values below 190 cm, in samples older than 2800 ^{14}C yr B.P., predate by centuries any known mining activities in Spain.

A comparison of the $\mathrm{Hg_T}$ profile with those of dried samples shows that some Hg was lost during heating. For example, the peak at 17 cm and the higher values of the deeper section of the core are represented entirely by Hg that volatilizes at the lowest temperature (30°C). Between 15 to 25 and 190 to 250 cm, peat layers contain Hg that has low thermal stability;

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