REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
30 October 1996

3. REPORT TYPE AND DATES COVERED
Technical

4. TITLE AND SUBTITLE
GALLIUM IMIDE, $\{Ga(NH)_{3/2}\}_n$, A NEW POLYMERIC PRECURSOR FOR GALLIUM NITRIDE POWDERS

5. FUNDING NUMBERS
•N00014-95-1-0194
R&T Project 3135008---16
•Dr. Harold E. Guard

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Chemistry
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8. PERFORMING ORGANIZATION REPORT NUMBER
Technical Report
No. DU/DC/TR-61

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
300 North Quincy Street
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

19961209 038

11. SUPPLEMENTARY NOTES
Accepted for publication in *Chemistry of Materials*

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for Public Release
Distribution Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

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14. SUBJECT TERMS
gallium, imide, precursor, gallium nitride, nanocrystalline

15. NUMBER OF PAGES
9

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
Unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT
Unclassified

20. LIMITATION OF ABSTRACT
Unlimited

NSN 7540-01-280-5500

DTIC QUALITY INSPECTED 3

Standard Form 298 (Rev 2-89)
Prescribed by ANSI Std Z39-18
298-102

OFFICE OF NAVAL RESEARCH

Grant N00014-95-1-0194
R&T Project 3135008---16

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Gallium Imide, $\{Ga(NH)_{3/2}\}_n$, a New Polymeric Precursor for Gallium Nitride Powders.

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The Group 13 derivatives, $M(NH_2)_3$, are advantageous precursors for conversion to Group 13 nitrides. They are likely to eliminate NH_3 at relatively low temperatures, possibly through a stepwise deamination shown in Equation 1, to afford solid state materials without major separation efforts. Since they do not contain organic groups they should, theoretically, yield pure nitride phases with minimum quantities of a residual hydrogen content, if any. In the relevant scientific literature, the $M(NH_2)_3$ derivatives are customarily called amides, $M(NH_2)(NH)$ - amide imides, and $M(NH)_{3/2}$ - imides.

$$M(NH_2)_3 \xrightarrow[\text{-}NH_3]{\Delta} M(NH_2)(NH) \xrightarrow[\text{-}1/2\ NH_3]{\Delta} M(NH)_{3/2} \xrightarrow[\text{-}1/2\ NH_3]{\Delta} MN \qquad (1)$$

For M = B, the ammonolysis of BX_3 (X = Cl, Br) was reported to yield $B(NH_2)_3$, and NH_4Cl;[1] however, a subsequent reinvestigation of this reaction both in the gas phase and in liquid NH_3 showed a polymeric solid with the approximate formula $B(NH)_{3/2}$.[2] Boron imide was also claimed in the ammonolysis of BI_3.[3] Also, the ammonolysis of the B-X bonds on the borazine ring resulted in the (polyborazinylamine) polymer of the formulation identical to that of boron imide.[2,4] On the other hand, transamination of 2,4,6-tris-(dimethylamine)borazine with ammonia lead to the formation of the postulated dimeric $\{[(NH_2)BNH]_3\}_2$.[5] For M = Al, the attempted synthesis of $Al(NH_2)_3$ through the metathetical reaction between $AlBr_3$ and KNH_2 or ammonolysis of $H_3Al{\bullet}NMe_3$ resulted at room temperature, in both cases, in the polymeric $\{Al(NH_2)(NH)\}_n$.[6] In the case of M = In, crystalline $In(NH_2)_3$, obtained from the metathetical reaction between InI_3 and KNH_2 in liquid NH_3, was claimed to be stable at ambient.[7] In the relevant case of M = Ga, it was stated that the reactions between $MGa(NH_2)_4$ and NH_4Cl (M = K, Na) gave $Ga(NH_2)_3$ as an amorphous product, which was thermally unstable with regard to NH_3 evolution.[8] However, the preparations of $MGa(NH_2)_4$ in liquid NH_3 required rather impractical reaction times.

One of the feasible routes to Group 13 amide imides and imides is transamination of the homoleptic compounds $[M(NR_2)_3]_n$ (n = 1, 2) with NH_3. In this regard, the volatile early transition metal and main group dialkylamide derivatives in combination with gaseous ammonia were demonstrated in vapor deposition techniques to yield nitride films.[9] Particularly, GaN and AlN were obtained from their dimethylamide derivatives via this route at 200-250 °C.[10] Based on both solution and gas phase studies, the presence of various amide and imide intermediate species was postulated in these reaction systems.[11] However, an ambient temperature stable form of an appropriate gallium derivative has not been reported to date. Described herein is a successful preparation of a new polymeric precursor with a formula corresponding to gallium imide, $\{Ga(NH)_{3/2}\}_n$, which, upon pyrolysis, yields nanosized cubic/hexagonal GaN solids.

We first explored the $GaBr_3/3LiNH_2$ system which, upon LiBr formation and its convenient removal by ether washings, was hoped to afford gallium amide. However, the reactions between $GaBr_3$ and $LiNH_2$ in refluxing aromatic/diglyme solvents yielded solids containing unreacted $LiNH_2$. The pyrolysis of these solids at 450 °C under vacuum resulted in the formation of GaN, as evidenced by XRD and IR spectroscopies, but sublimable NH_4Br was also formed, and some lithium and bromine were retained in the final product mixture. Similar results were obtained from combinations of $GaBr_3$ and $LiNH_2$ in liquid NH_3 followed by pyrolysis at 450 °C; this path was complicated by sublimation of volatile $Br_3Ga{\bullet}nNH_3$ from the hot zone of the heated set-up. We also used $Br_3Ga{\bullet}nNH_3$, instead of $GaBr_3$, in refluxing solvent systems (as above) and still obtained products containing GaN but contaminated with non-removable lithium and bromine species. Unfortunately, this metathetical reaction system did not yield pure gallium amide or imide precursors and, consequently, pure GaN was not produced under the range of applied conditions.

A successful preparation of the precursor with the formula corresponding to gallium imide, $\{Ga(NH)_{3/2}\}_n$ (**1**), was accomplished by reactions of $[Ga(NMe_2)_3]_2$[12] (**2**) with gaseous NH_3[13] or liquid NH_3.[14] The estimated quantity of the evolved $HNMe_2$ indicated a very efficient transamination of **2** towards an imide type of product and only residual $-NMe_2$ groups remained in the solid. This was further corroborated by IR spectroscopy that showed no discernible C-H bands for both solids. However, the elemental analyses of the solids showed 2.49 to 3.65% carbon content supporting small quantities of these groups. The N/Ga and H/N element ratios of nearly 1.5/1 and 1/1, respectively, were consistent with the imide formulation for precursor **1**. The IR spectra for the solids were in agreement with such a formulation and the broadness of the bands suggested a polymeric nature for the imide. The bands at approx. 3150 cm^{-1} and 1515 cm^{-1} could be assigned, respectively, to the stretching and bending modes of the -N(H)- moieties.[6b] The very strong band at approx. 570 cm^{-1} was typical of the Ga-N stretch.[15a] However, the weak band at approx. 1615 cm^{-1} suggested the presence of some strongly adsorbed NH_3 molecules[15b] or -NH_2 groups.[6b] This band diminished in intensity after a prolonged evacuation of the solid at ambient temperatures, which was consistent with progressing deamination and supported the above assignment. Finally, the observed total weight loss of 4.9% in the TGA experiment (UHP nitrogen) for solid **1** could be compared with the theoretical value of 9.2% for: $Ga(NH)_{3/2} = GaN + 1/2\ NH_3$. In this regard, it was noticed that solid **1** was extremely sensitive to oxidation; an initial fast weight increase was observed beginning at 30 °C to 100 °C even with application of the UHP nitrogen carrier gas. The overlap of the oxidation (weight increase) and deamination (weight loss) could explain the observed low weight loss. However, the magnitude of the weight changes in the TGA experiment compared favorably with the imide formulation for precursor **1.**

The pyrolysis studies (450-500 °C, vacuum or NH_3 flow) were performed for precursor **1** obtained both from the reaction of compound **2** with NH_3 in the liquid phase[16] and in the gas phase to yield similar results. The former case will be discussed below in more detail. Thus, the elemental analyses of the solids from pyrolysis of **1** under vacuum and under NH_3 showed the N/Ga atomic ratios were very close to 1/1, consistent with the formation of stoichiometric GaN and only small quantities of retained carbon (e.g. 0.22%, pyrolysis under NH_3). Interestingly, for pyrolysis of **1** under vacuum, the analysis of collected volatiles showed a small amount of CH_4 (and, possibly, H_2) and $HNMe_2$ in addition to the major NH_3 component. The IR spectroscopy supported the formation of GaN in all investigated materials (strong Ga-N band at 570 cm^{-1}).[15a] The presence of the weak bands at 3200 cm^{-1} and 980 cm^{-1}, especially for the pyrolysis product under vacuum, could be due to remaining -N(H)- and -GaN(H)- species; however, some N-C species from the cracking of the residual -NMe_2 groups (evidenced by CH_4 evolution) could contribute to the latter band.

The gray-yellowish (pyrolysis under vacuum) and yellow-grayish (pyrolysis under NH_3) products were shown by XRD spectroscopy (Fig. 1) to be, remarkably, the same mixture of cubic and hexagonal close-packed layers of GaN that was reported earlier by Gladfelter et al.[17] from thermal decomposition of $[H_2GaNH_2]_3$. The relatively sharp XRD powder pattern obtained for the solid from the pyrolysis at 500 °C under NH_3 (Fig. 1A) matched the pattern reported in the above reference. The TEM micrograph and the electron diffraction pattern for this solid supported the presence of relatively large particles of cubic GaN (Fig. 2A). The observed cross-fringes (approx. 71° angle of the (111) planes viewed along the [110] direction) were consistent with the cubic form of GaN. Based on the relative broadness of the XRD powder patterns (Scherrer's equation) and the TEM results (Fig. 2), the solid from the pyrolysis at 500 °C under NH_3 consisted of bigger and less disordered GaN crystallites (av. 7 nm) than the solid from the pyrolysis at 450 °C under vacuum (av. 2 nm). A topotactic relationship between the precursor $[H_2GaNH_2]_3$ and the final product was proposed to play a role in the formation of the kinetically favored cubic GaN as compared with the nitride's thermodynamically stable and common hexagonal form.[17] However, in the case of gallium imide this premise could not be ascertained due to the lack of detailed knowledge of the polymeric imide's structure.

In addition to the discussed pyrolysis schemes, refluxing precursor **1** in N,N,N',N'-tetramethyl-1,6-hexanediamine (b.p. 210 °C) for 40 h and removing the solvent afforded a pale yellow solid that displayed an XRD powder pattern similar to the pattern for the solid heated at 450 °C under vacuum. The TEM images showed this solid to consist of very small crystallites, < 1nm (Fig. 2C). Also, heating pure compound **2** under NH_3 using a specially designed temperature program resulted in a yellow material that gave an XRD powder pattern identical with the ones discussed above.

We also report preliminary results on the preparation and utilization of yet another imide-type precursor to GaN. It was obtained from an oily product synthesized in the reaction between $GaCl_3$ and $LiNEt_2$, which was aimed at the synthesis of $\{Ga(NEt_2)_3\}$. This oily product reacted with NH_3 to afford a yellow solid that showed similar IR and TGA characteristics as precursor **1.** This solid was also converted by pyrolysis under ammonia to the same type of the cubic/hexagonal GaN as discussed above.

In summary, an efficient preparation of the new polymeric gallium imide, $\{Ga(NH)_{3/2}\}_n$, from the reactions between $[Ga(NMe_2)_3]_2$ and NH_3 at ambient temperatures was described. The gallium imide precursor was shown to yield upon pyrolysis a rare cubic/hexagonal variety of GaN. Some control of the average particle size of GaN in the nanosized region was achieved by application of various pyrolysis schemes.

Acknowledgment. We wish to thank the Air Force Office of Scientific Research and the Office of Naval Research for their financial support.

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(13) 0.204 g of **2** (0.5 mmol) and 2.3 mmol of NH_3 (dried over Na) were combined at r.t. for 16 h. Determination of gas products (calibrated manifold and IR calibration curves): total volatiles, 3.1 mmol; NH_3, 0.6 mmol; $HNMe_2$, 2.5 mmol (by difference). Off-white solid product: IR (KBr, cm^{-1}): 3150 (m,br), 1615 (w), 1511 (m,br), 1300 (vw), 990 (s,br), 550 (vs,br). For a similar reaction carried out with larger excess of NH_3 (1 mmol of **2** and 15.7 mmol of NH_3): yellowish solid product: IR (KBr, cm^{-1}): 3140 (m,br), 1500 (m,br), 1309 (vw), 979 (s,br), 560 (vs,br); EA (%): Ga, 68.82; N, 22.06; C, 3.65; H, 2.17; N/Ga = 1.60/1.00; H/N = 1.36/1.00.

(14) About 50 mL of liquid NH_3 (dried over Na) was transferred at -78 ^{o}C onto 1.02 g of **2** (5.0 mmol) in an evacuated flask. Ammonia was refluxed for 8 h and evaporated to afford an off-white solid. The solid was further evacuated for 3 h: EA (%): Ga, 67.00; N, 21.02; C, 3.01; H, 2.30; N/Ga = 1.56/1.00; H/N = 1.50/1.00; IR (KBr, cm^{-1}): 3150 (s,br), 1615 (w), 1515 (m,br), 1307 (w), 989 (s,br), 585 (vs,br), and for 16 h: EA (%): Ga, 64.54; N, 20.10; C, 2.49; H, 1.68; N/Ga = 1.55/1.00; H/N = 1.16/1.00; IR (KBr, cm^{-1}): 3130 (m,br), 1631 (vw), 1516 (m,br), 1310 (vw), 985 (m,br), 569 (vs,br); TGA (weight loss): 30-240 ^{o}C, 4.6%; 240-450 ^{o}C, 0.3%; total, 4.9% (gray-yellow residue).

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(16) Pyrolysis (500 ^{o}C, NH_3 flow, 6 h) of **1** obtained from reaction in liquid NH_3: EA (%): Ga, 81.02; N, 15.87; C, 0.22; H, 0.54; N/Ga = 0.98/1.00; IR (KBr, cm^{-1}): 975 (vw,br), 570 (vs,br); XRD (Fig. 1A); TEM image and electron diffraction pattern (Fig. 2A). Pyrolysis (450 ^{o}C, vac., 4 h) of **1** obtained from reaction in liquid NH_3: sample

weight, 0.33 g; determination of gas products (calibrated manifold and IR calibration curves): non-condensables (CH_4+H_2), 0.06 mmol; condensables, 1.6 mmol (NH_3, 1.6 mmol; $HNMe_2$, < 0.1 mmol); mass of final product, 0.29 g or ceramic yield of 87.9%; expected yield for $Ga(NH)_{3/2}$ = GaN + 1/2 NH_3, 90.8%; EA (%): Ga, 76.01; N, 14.58; C, 0.97; H, 0.57; N/Ga = 1.05/1.00; IR (KBr, cm^{-1}): 3200 (w,br), 984 (m,br), 570 (vs,br); XRD (Fig. 1B); TEM image and electron diffraction pattern (Fig. 2B).

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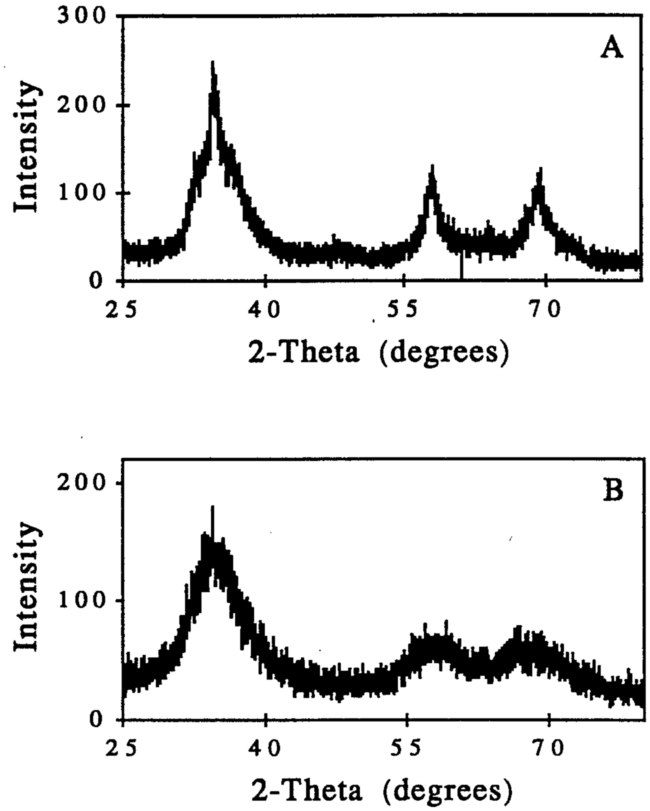
Legend of Figures

Figure 1. X-ray powder diffraction patterns for pyrolysis products of $\{Ga(NH)_{3/2}\}_n$ (**1**). **A** - 500 °C, NH_3 flow; **B** - 450 °C, vacuum.

Figure 2. TEM images and electron diffraction ring patterns for particles of GaN from pyrolysis of $\{Ga(NH)_{3/2}\}_n$ (**1**); **A** - 500 °C, NH_3 flow; **B** - 450 °C, vacuum; **C** - reflux in N,N,N',N'-tetramethyl-1,6-hexanediamine, b.p. 210 °C.


A
300
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Intensity
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B
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Intensity
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Figure 1

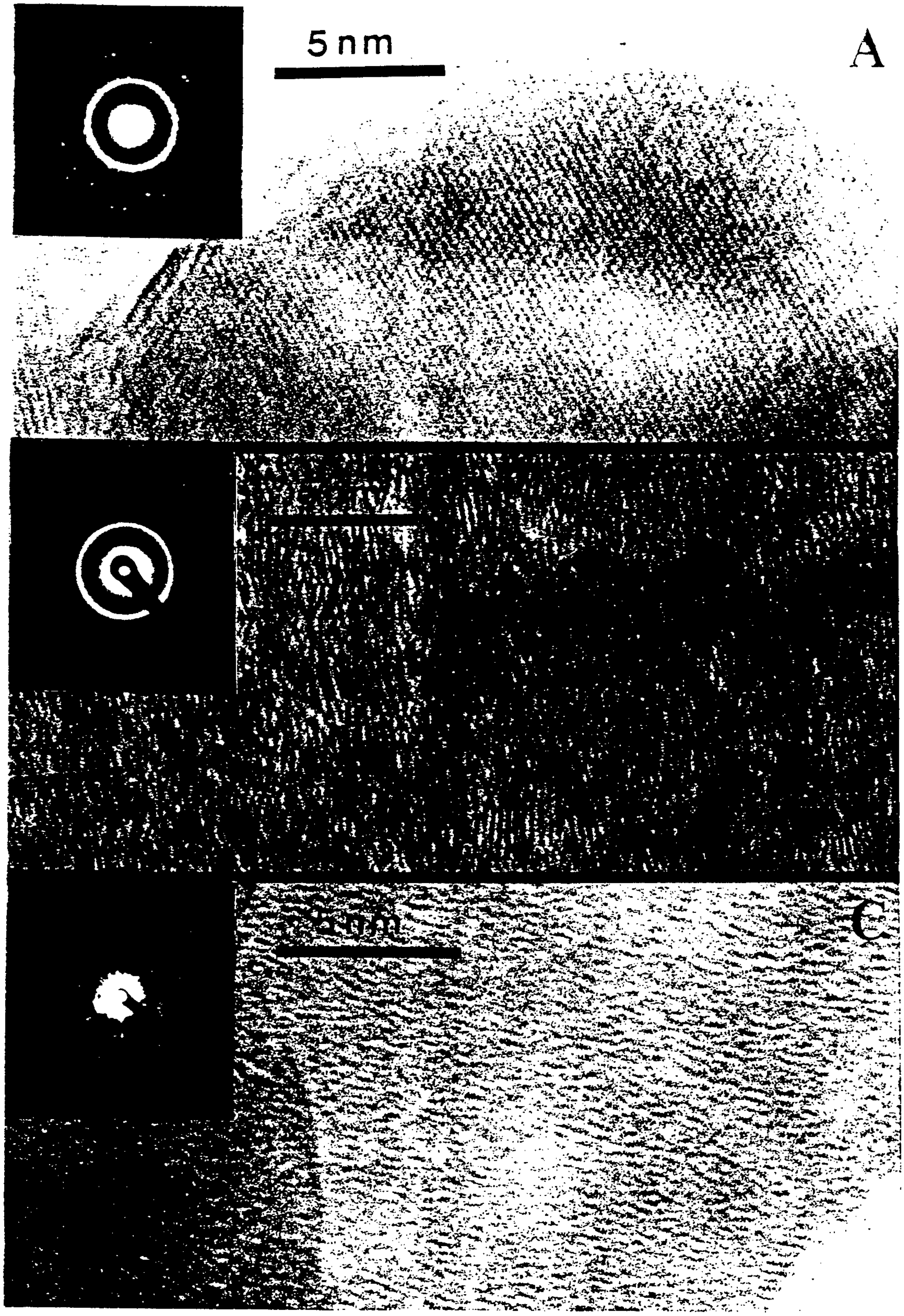

Figure 2

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