Synthetic Route of Layered Titanium Nitride Chloride TiNCl Using Sodium Amide

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ABSTRACT: A synthetic route in a closed system for layered titanium nitride chloride TiNCl has been developed using sodium amide NaNH2 as a nitrogen source. A highly crystalline sample is obtained by an appropriate thermal decomposition of aminated titanium chloride. The obtained TiNCl was also characterized using electronic resistivity measurement and photoemission spectroscopy. TiNCl showed hopping conduction compatible with an in-gap state revealed by photoelectron spectroscopy. However, it appeared highly electron-doped, albeit without showing superconductivity. Comparison with the spectrum of superconducting sodium-doped samples suggests the presence of the microstructure required to exhibit superconductivity.

1. INTRODUCTION

Layer-structured ternary metal nitride halides MX3 (M = Ti, Zr, Hf; X = Cl, Br, I) contain two polymorphs, the α-form and β-form, with different metal nitride networks.1 Both are band insulators and are changed into superconductors with moderately high transition temperatures upon electron doping. It is well known that lithium-intercalated β-form HfNCl is a superconductor with a transition temperature \( T_c \) as high as \( \sim 26 \) K.1−3 The superconductivity in the β-form compounds has been studied extensively. The mechanism reported is not easy to interpret all the experimental results consistently by a conventional phonon-mediated Bardeen Cooper Schrieffer mechanism.4−7 On the other hand, the α-form compound, TiNCl, also shows superconductivity at \( T_c \sim 16 \) K after electron doping by intercalating alkali or alkaline earth metals and/or organic bases.8−10 The importance of interlayer coupling was reported for pairing:11,12 the superconducting characteristics are significantly different from the β-type. A comparison of the superconductivity in different M-N networks will be interesting.

In a study on a superconducting mechanism, the isotope effect on \( T_c \) provides crucial evidence of whether electron–phonon interaction is responsible for the superconductivity. However, synthesizing TiNCl has several issues that hinder the investigation of the effect. TiNCl is easily hydrogen-reduced and decomposed into TiN at a temperature ranging from 400 to 450 °C.13 In addition, it cannot be obtained by the reaction within a sealed metal or metal hydrides with NH4Cl because TiH2 is stably formed at 400 °C, unlike the other layered nitride halides such as Zr/HfNCl.1,2 Then, TiNCl was conventionally prepared by the thermal decomposition of TiCl4 under NH3 gas flow in an open system with a vertical reaction cell,8,14 but retaining the ^15N isotope using NH3 gas as a nitrogen source is extremely difficult or almost impossible realistically.

In a conventional reaction, large amounts of intermediates such as titanium amides, NH4Cl, and \((\text{NH}_4)_2\text{TiCl}_6\) are produced with an intense exothermic reaction. These intermediates are gradually heated up to 400 °C under the NH3 stream and maintained at that temperature for several hours to purge the excess compounds; a low crystalline TiNCl precursor is left at the bottom of the reaction cell. The precursor is sealed together with a small amount of the transporting agent NH4Cl and then purified by chemical vapor transport as highly crystalline TiNCl.8 Considering the above synthesis process, if the TiNCl precursor could be formed using a solid reagent other than gaseous NH3 as a nitrogen source in a closed reaction cell, an essential technique for synthesizing ^15N substituents would be developed. It could help not only to elucidate the superconducting mechanism of TiNCl but also to investigate the isotopic effect of other metal nitride superconductors.
NaNH₂ is a highly reactive solid nitrogen source used for the combustion reaction with 3d transition-metal chlorides to obtain metal nitrides.15,16 The reactions are thermodynamically driven by a metathesis reaction involving the formation of stable NaCl. NaCl does not contribute to chemical transport; if the reaction with TiCl₄ can be controlled, TiNCl may be obtained in a sealed glass tube. In this study, a synthetic route for highly crystalline TiNCl has been developed using NaNH₂ in a sealed Pyrex glass tube without an NH₃ gas stream. The chemical state of such obtained semiconducting TiNCl was characterized using photoemission spectroscopy and compared with conventionally obtained TiNCl.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. TiCl₄ (Aldrich, >99.0%) and NaNH₂ (Wako, 90.0+%) were mixed under dry nitrogen gas and then sealed into an evacuated glass tube. Vacuum sealing was performed by freezing the sample part with liquid nitrogen to prevent the volatilization of TiCl₄. Caution! An intense exothermic reaction occurs when these reagents are mixed. Synthesis using a large amount of the starting materials may cause a severe accident with an explosive reaction. The typical amount of TiCl₄ and NaNH₂ used was about 2 mL and 0.2 g, respectively, using a glass tube with an inner diameter of 8 and 200 mm in length. There is a risk of explosion of HCl and NH₃ gases during release. Wear protective glasses during the experiment.

2.2. Characterization. The infrared (IR) spectrum was measured by a KBr disk using a Shimadzu IRAffinity-1 spectrometer. Thermogravimetric analysis was performed by maintaining the temperature at each value for 15 min while evacuating and then taking it out from the reaction cell while flowing dry nitrogen gas and measuring the mass. Heating was performed at a heating rate to reach the target temperature within a few minutes. Powder X-ray diffraction (XRD) measurements were carried out using an imaging plate Guinier camera (Huber, model 670G) with Mo Kα radiation (λ = 0.709260 Å) and a rotating goniometer, where the sample was sealed in a thin Pyrex glass capillary. A TOPAS-Academic software package was used for the Rietveld analysis.17 A backscattered electron (BSE) image and the energy-dispersive X-ray spectra were observed using a scanning electron microscope (JEOL, JSM-6010LA). Electrical resistance was measured by an electrode-insertion type diamond anvil cell used as a resistance detector for microcrystals. Magnetic susceptibility was measured using a superconducting quantum interference device magnetometer (Quantum Design) under zero-field cooling and field cooling with an applied magnetic field of 10 Oe.

Hard X-ray photoelectron spectroscopy (HAXPES) measurements were performed at the beamline 47XU of SPring-8 at room temperature with hν = 7.94 keV photons, and the total energy resolution was set to 0.25 eV.19,20 All samples were transported to the equipment without exposure to air, and then they were fractured under a pressure of 10⁻⁶ Pa to obtain a clean surface. The binding energy was calibrated using the Fermi edge of Au.

3. RESULTS AND DISCUSSION

3.1. Synthesis of TiNCl Using NaNH₂. 3.1.1. Preliminary Reaction of TiCl₄ with NaNH₂. The sealed glass tube containing TiCl₄ and NaNH₂ was gradually heated up to 150 °C for 12 h and then kept at this temperature for 1–2 days. Prolonged heating was found to be favorable to the reaction. It is essential to react sufficiently at a lower temperature than 200 °C to prevent the volatilization of TiCl₂ and the explosion of the glass tube. Hereafter, the resulting solid is called the preliminary reacted solid.

3.1.2. Direct Heating of the Preliminary Reacted Solids. The preliminary reacted solid was directly heated around 400 °C in the as-sealed form. The heating treatment did not result in TiNCl, but (NH₄)₂TiCl₆ and low crystalline TiN were recovered instead. It showed the same result as with the chemical transport. The existence of (NH₄)₂TiCl₆ indicates that the remaining TiCl₂ has reacted with NH₄Cl upon further heating NH₄Cl. NH₄Cl can be produced by the reaction of TiCl₂ and NH₃ emitted by the decomposition of NaNH₂.

On the other hand, the production of TiN suggests that a Ti–NH₂ bond replaced at least one Ti–Cl bond in TiCl₄; possibly, a titanium amide chloride such as TiCl₄(NH₂)₃ is generated before the heating process. This TiCl₄ ammonolysis reaction is energetically favorable.21,22 TiCl₄ forms ammonia-incorporated complexes with the TiCl₄·xNH₃ gross composition, and heating the complexes in an ammonia-rich atmosphere results in the stepwise amimation of TiCl₄ to finally form TiCl(NH₂)₃.13,25,26

3.1.3. IR Study of the Preliminary Reacted Solids. The IR spectrum of the preliminary reacted solids was measured to examine the reaction of TiCl₄ with NaNH₂, as shown in Figure 1. Three prominent absorption bands were observed in the spectrum. The frequencies around 3200 and 1400 cm⁻¹ are close to those of vibrational modes of NH₄⁺ and/or NH₃· stretching of the ammine complexes; then, they were assigned to N–H···H and N–H deformation vibrations, respectively.25 The XRD measurement of the same solid shows a mixture pattern of NaCl and other unknown phases with relatively broad peaks, but no NH₄Cl has been observed. This finding indicates that the absorption bands are attributed to the ammonia complexes of titanium chloride, such as TiCl₄·xNH₃.

One more IR absorption band could be assigned to the −NH₂ groups, which has been reported to appear at a frequency of 1550 cm⁻¹.16,26 It has been reported that the heating of the ammonia complexes TiCl₄·xNH₃ gradually decreases its ammonia content and results in the stepwise amination of TiCl₄.26 It is reasonable that the preliminary
reacted solids contain TiCl₃(NH₂), TiCl₄(NH₂)₂, and TiCl₄(NH₂)₃, together with TiCl₃xNH₃. Namely, the reaction at this process can be written as the equation TiCl₄ + NaNH₂ → TiCl₃(NH₂) + NaCl in the simplest case.

3.1.4. Thermogravimetric Study of the Preliminary Reacted Solids. As expected in the zirconium analogue, the amide TiCl₃(NH₂) would thermally decompose into TiNCl.²⁹ Since TiNCl was not transported from the as-obtained mixture described in Section 3.1.2, some reaction factors impede the chemical transport at around 400 °C. Thermogravimetric analysis while evacuating was performed on the preliminary reacted solids, as shown in Figure 2. On evacuation up to 180 °C, the solids lost their weight gradually. The initial state comprises aminated TiCl₄, NaCl, TiCl₄xNH₂, and a small amount of unreacted NaNH₂. In the literature of ref 26, TiCl₄xNH₂ (most stably x = 8) releases its ammonia content to the minimum x = 2 in the vacuum treatment even at room temperature. NaNH₂ shows a slight N₂ emission below 230 °C.³⁰ The weight reduction factor below 180 °C in this study is mainly attributed to the aminated TiCl₄ decomposition. The simplest reaction in this stage can be written as an equation

TiCl₄(NH₂) + NaCl → TiNCl + NaCl + 2HCl  

(1)

The weight loss for this reaction was calculated to be 32%. It should be increased if the stepwise amination has much proceeded according to the following equations

TiCl₄(NH₂)₂ → TiNCl + HCl + NH₃  

(2)

TiCl(NH₂)₃ → TiNCl + 2NH₃  

(3)

and so forth. However, the actual weight loss W₁ was only 9.2%. This result indicates that the reaction had not completed at this temperature but would continue to a much higher temperature.

The second decomposition stage, accompanied by a steep weight loss beginning from 180 °C, has been observed up to 300 °C, and the decomposition seems to complete at this temperature. A similar thermogravimetric curve for the zirconium analogue was observed in the literature, and the following equation was proposed: 2ZrCl₄(NH₂) → ZrNCl + ZrCl₄ + NH₃Cl.²⁹ On further heating up to 800 °C, the sample was decomposed to ZrN. In the present study, the decomposition temperature of TiNCl can be considerably lower than that of ZrNCl, especially if the unreacted NaNH₂ exists as an even stronger reducing reagent. Then, the following reaction would have simultaneously occurred with reaction 1 above 200 °C: 8TiNCl → 2TiCl₄ + 6TiN + N₂. The weight loss for this reaction was calculated to be 52%. Although this value is in good agreement with the amount of the loss W₂ (49%), the quantitative analysis of this stage is much more complicated since reactions 2 and 3 should have occurred in parallel under the evacuation condition, which resulted in a significant weight loss.

3.1.5. Procedures to Obtain TiNCl. From these results, while the preliminary reacted solids include Ti–NH₂ bonds, they contain unreacted TiCl₄ and other ammonia complexes of TiCl₄. The procedures to obtain TiNCl using NaNH₂ can be proposed as follows. (1) The sealed mixture of TiCl₄ + NaNH₂ sufficiently reacts around 160 °C to obtain preliminary reacted solids. (2) The seal is opened, and unreacted TiCl₄ is purged from the glass tube. Then, the preliminary reacted solids are evacuated again with an elevated temperature of 180 °C to remove HCl from TiCl₄(NH₂) and/or other aminated compounds. Here, we can obtain a low-crystallinity (LC) TiNCl with the whole equation in the simplest case written in TiCl₄ + NaNH₂ → TiCl₄(NH₂) + NaCl → TiNCl + NaCl + 2HCl. (3) The heating and evacuation should be stopped before decomposition to TiN occurs and sealed again into a glass tube. (4) The glass tube sends chemical transport to obtain highly crystalline (HC) TiNCl.

3.1.6. Chemical Vapor Transport of TiNCl. The following equation can simply describe the net chemical transport in the transport reaction will proceed simply by sealing the resulting LC-TiNCl-containing materials as they are. A small amount of NH₄Cl may be added as a transport agent. The transport reaction occurs in the higher-temperature zone. When the glass tube was put into a horizontal furnace at a temperature gradient of 400–230 °C, the purified and highly-crystalline (HC) TiNCl was successfully obtained, as shown in the XRD pattern of Figure 3 and the BSE image of Figure S1. The crystallographic parameters were refined within a single

Figure 2. Thermogravimetric curve for the preliminary reacted solids measured in vacuum.

Figure 3. Rietveld analysis of the XRD pattern of TiNCl obtained in the process proposed in this study. Open circles show the observed data points, and the solid line represents the calculated diffraction pattern. The tip marks are the calculated 2θ angles for the Bragg peaks of TiNCl.
Third, the prominent peaks of TiNCl_A shift to the higher binding energy side about 0.3 eV compared to TiNCl_C, even though the sample was not a Na-doped one. The same chemical shift is also observed in the core-level spectrum of the other elements N 1s and Cl 2p (Figure S4). These three findings suggest that TiNCl_A seems to be highly electron-doped. Surprisingly, the peak shape of TiNCl_A is quite similar to sodium-intercalated TiNCl prepared from the conventional way (denoted as Na0.1TiNCl) when the peaks shifted 0.3 eV to the higher binding energy side. The intercalation compound Na0.1TiNCl shows superconductivity around 16 K, however, TiNCl_A did not show any specific magnetic signals down to 1.8 K unless intercalated (Figure S5). This result suggests an essential difference in the electronic structure of TiNCl_A and Na0.1TiNCl.

Carefully comparing the core-level spectrum of Ti 2p of these samples, another fine structure around 455.5 eV (indicated by arrows in Figure 4b) emerges other than the shoulder-like component of the main structure of Na0.1TiNCl. Although the area of the fine structure is small, peak fitting can be performed reliably, as shown in Figure S5. We can see a small contribution of component D in the peak fitting of Na0.1TiNCl. However, it could not be observed in pristine TiNCl_A despite its highly electron-doped state. It did not appear unless the sample was Na-doped (Figure S5).

On the other hand, the structure around 457 eV (denoted as component A) mainly corresponds to the amount of Ti3+ content in the sample. Since the electron doping should increase the Ti3+ content, component A was found in TiNCl_A and TiNCl_C even in the pristine compound, and it increased monotonically with the Na concentration. Considering that all Na-doped samples exhibit superconductivity, it is very plausible that component D is necessary for the appearance of superconductivity. This finding is essential to clarify the electronic state required for superconductivity for this group of materials. Further precise measurements and theoretical studies are required.

However, it is still unclear why such highly electron-doped TiNCl was obtained. It is reasonable that it is due to a property peculiar to the synthetic route in this study, namely, the usage of NaNH2. Some unreacted NaNH2 remaining in the reaction cell may cause another reaction besides the proposed ideal reactions. The decomposition of NaNH2 alone hardly occurs at 230 °C, but the reaction can proceed even at a lower temperature at the most reactive interface of the solids in contact. This reaction would release NaH, NH3, H2, and N2 as the intermediate product. There is another report that adding NaH to NaNH2 suppresses the generation of ammonia and release H2.35 The partial pressure of NH3 is suppressed in the decomposition process, and the reaction may occur in the presence of H2 or N2 gas instead. It might cause hydrogen incorporation into the obtained TiNCl. In ZrNCl, it has been reported that the incorporated hydrogen atoms sit around N atoms with a suggestion of carrier number change.31 The same intercalation might happen in TiNCl, bringing a slight difference in the coordinating position of N atoms, and may influence the carrier number, resulting in high electron doping. This side reaction is not easy to control, and these complicated reaction processes may be a factor that give an electronic state different from that of TiNCl obtained by the conventional method. It is suggested that the atmosphere during chemical transport strongly affects the quality of the sample. The other

Figure 4. (a) Ti 2p core-level spectra of TiNCl obtained in this study (TiNCl_A) compared with that obtained using the conventional method (TiNCl_C) together with intercalated samples (Na0.1TiNCl). Each spectrum was normalized by the area of the peak. (b) Enlargement of the fine structure around 455.5 eV.

The temperature dependence of resistance of TiNCl_A is closer to hopping conduction,32 suggesting an in-gap state near the Fermi level (E_F). This finding infers some impurities around N atoms, and the X-ray structural analysis supports it.

HAXPES was used to elucidate the chemical state of TiNCl_A compared with TiNCl_C. This measurement indicates the following three things. First, the top of the valence band of TiNCl_A lies at ~1.5 eV, comparable to the previously reported value (Figure S3).33 There is a tiny intensity at the E_F, appearing as a localized state. This fact is compatible with the semiconductor-like properties of hopping conduction suggested by the resistivity measurement.

Second, the Ti 2p HAXPES spectrum consists of two peaks at around 457.5 and 463.5 eV, corresponding to the spin–orbit split of Ti 2p1/2 and Ti 2p3/2 respectively, as shown in Figure 4a. The Ti 2p1/2 peak has a broad shoulder-like component in the lower binding energy side, similar to the valence splitting of previously reported electron-doped samples.33,34

Third, the prominent peaks of TiNCl_A shift to the higher binding energy side about 0.3 eV compared to TiNCl_C, even though the sample was not a Na-doped one. The same chemical shift is also observed in the core-level spectrum of the other elements N 1s and Cl 2p (Figure S4). These three findings suggest that TiNCl_A seems to be highly electron-doped. Surprisingly, the peak shape of TiNCl_A is quite similar to sodium-intercalated TiNCl prepared from the conventional way (denoted as Na0.1TiNCl) when the peaks shifted 0.3 eV to the higher binding energy side. The intercalation compound Na0.1TiNCl shows superconductivity around 16 K, however, TiNCl_A did not show any specific magnetic signals down to 1.8 K unless intercalated (Figure S5). This result suggests an essential difference in the electronic structure of TiNCl_A and Na0.1TiNCl.

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sample morphology-dependent functionalities might also be expected in the present pristine TiNCl.

4. CONCLUSIONS

We prepared a HC TiNCl using a reaction of TiCl4 with NaNH2 in a closed system. This report is the first example of synthesizing TiNCl in a closed system, which requires high-level technical skills to synthesize even by conventional methods. This technique can maintain the initial nitrogen source and is necessary to investigate the 15N isotope effect for elucidating the superconducting mechanism. It could be carried out not only for TiNCl but also for the other metal nitride superconductors. Furthermore, the obtained TiNCl appeared highly electron-doped, albeit without showing superconductivity. Comparison with the spectrum of superconducting sodium-doped samples suggests the presence of a microstructure required to exhibit superconductivity. It may be a clue to elucidate the mechanism of superconductivity, which has been unsolved for more than 10 years since it was discovered in 2009.8

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c06986.
Details of crystallographic parameters and additional experimental results, including a typical image of the sample crystals (PDF)

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Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsomega.1c06986

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors express our immeasurable gratitude to Emeritus Professor Shoji Yamanaka of Hiroshima University for his helpful suggestions throughout this study. The authors also thank Associate Professor E. Mouri and Professor T. Nakato of the Kyushu Institute of Technology for supporting the IR measurement and acknowledge A. Yasui, Y. Takagi, M. Matsumoto, and Y. J. Li for their partial support for the PES experiment. The synchrotron radiation experiments were performed at BL47XU in SPring-8 (proposal no. 2020A0846). This work has been partly supported by the Japan Society for the Promotion of Science (JSPS) through its JSPS KAKENHI grant nos. JP18KK0076, JP18H01709 and the Fund for the Promotion of Joint International Research (B) (JP18KK0076) from the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT).
REFERENCES

(1) Yamanaka, S. Intercalation and Superconductivity in Ternary Layered Structured Metal Nitride Halides (MNX: M = Ti, Zr, Hf; X = Cl, Br, I). J. Mater. Chem. 2010, 20, 2922–2933.

(2) Yamanaka, S.; Hotehama, K.-i.; Kawaij, H. Superconductivity at 25.5K in Electron-Doped Layered Hafnium Nitride. Nature 1998, 392, 580–582.

(3) Zhang, S.; Tanaka, M.; Zhu, H.; Yamanaka, S. Superconductivity of Layered β-HfNCl with Varying Electron-Doping Concentrations and Interlayer Spacings. Supercond. Sci. Technol. 2013, 26, 085015.

(4) Kasahara, Y.; Kuroki, K.; Yamanaka, S.; Taguchi, Y. Unconventional Superconductivity in Electron-Doped Layered Metal Nitride Halides MXN (M = Ti, Zr, Hf; X = Cl, Br, I). Phys. C 2015, 514, 354–367.

(5) Taguchi, Y.; Kabwata, T.; Takano, T.; Kitora, A.; Kato, K.; Takata, M.; Iwasa, Y. Isotope Effect in LixZnNCl Superconductors. Phys. Rev. B: Condens. Matter Mater. Phys. 2007, 76, 064508.

(6) Tou, H.; Maniwa, Y.; Koiwasaki, T.; Yamanaka, S. Unconventional Superconductivity in Electron-Doped Layered $La_{1-x}(THF),HNCl$. Phys. Rev. Lett. 2001, 86, 5775–5778.

(7) Kuroki, K. Spin-Fluctuation-Mediated $d+id'$ Pairing Mechanism in Doped $\beta$-MNCl (M=Hf, Zr) Superconductors. Phys. Rev. B: Condens. Matter Mater. Phys. 2010, 81, 104502.

(8) Yamanaka, S.; Yasunaga, T.; Yamaguchi, K.; Tagawa, M. Structure and Superconductivity of the Intercalation Compounds of TiNCl with Pyridine and Alkali Metals as Intercalants. J. Mater. Chem. 2009, 19, 2573–2582.

(9) Zhang, S.; Tanaka, M.; Yamaguchi, S. Superconductivity in Electron-Doped Layered TiNCl with Variable Intercalator Coupling. Phys. Rev. B: Condens. Matter Mater. Phys. 2012, 86, 024516.

(10) Yamanaka, S.; Umemoto, K.; Zheng, Z.; Suzuki, Y.; Matsu, M.; Toyota, N.; Inumaru, K. Preparation and Superconductivity of Intercalation Compounds of TiNCl with Aliphatic Amines. J. Mater. Chem. 2012, 22, 10752–10762.

(11) Zhang, S.; Tanaka, M.; Yamanaka, S. Superconductivity in Electron-Doped Layered TiNCl with Variable Intercalator Coupling. Phys. Rev. B: Condens. Matter Mater. Phys. 2012, 86, 24516.

(12) Kusakabe, K. Pair-Hopping Mechanism of Superconductivity Activated by the Nano-Space Layered Structure. J. Phys. Chem. Solids 2012, 73, 1546–1549.

(13) Sasaki, Y.; Matsuizaki, R.; Yajima, A.; Akiyama, M. Reaction Process of Titanium Tetrachloride with Ammonia in the Vapor Phase and Properties of the Titanium Nitride Formed. Bull. Chem. Soc. Jpn. 1982, 55, 3193–3196.

(14) Juza, R.; Heners, J. Über Nitridhalogenide des Titans und Zirkons. Z. Anorg. Allg. Chem. 1964, 332, 159.

(15) Odahara, J.; Sun, W.; Muraoka, Y.; Yokoya, T.; Tadanaga, K.; Akiyama, M. Reaction Process of Titanium Tetrachloride with Ammonia in the Vapor Phase and Properties of the Titanium Nitride Formed. Bull. Chem. Soc. Jpn. 1982, 55, 3193–3196.

(16) Miura, A. Low-Temperature Synthesis and Rational Design of Nitrides and Oxynitrides for Novel Functional Material Development. J. Ceram. Soc. Jpn. 2017, 125, 552–558.

(17) Coelho, A. TOPAS-Academic V6: General Profile and Structure Analysis Software for Powder Diffraction Data; Coelho Software, Brisbane, Australia. http://www.topas-academic.net/.

(18) Matsumoto, R.; Sasama, Y.; Fujioka, M.; Iriume, T.; Tanaka, M.; Yamaguchi, T.; Takeya, H.; Takano, Y. Note: Novel Diamond Anvil Cell for Electrical Measurements Using Boron-Doped Metallic Diamond Electrodes. Rev. Sci. Instrum. 2016, 87, 076103.

(19) Ikegami, E.; Kobata, M.; Matsuda, H.; Sugiyama, T.; Daimon, H.; Kobayashi, K. Development of High Lateral and Wide Angle Resolved Hard X-Ray Photoemission Spectroscopy at BL47XU in SPring-8. J. Electron Spectros. Relat. Phenomena 2013, 190, 180–187.

(20) Ikegami, E.; Yasui, A.; Kawamura, N.; Mizumaki, M.; Tsutsui, S.; Mimura, K. Hard X-Ray Photoemission Spectroscopy at Two Beam Lines of SPring-8: Current Status and Ongoing Developments. Synchrotron Radiat. News 2018, 31, 10–15.

(21) Cross, J. B.; Schlegel, H. B. Molecular Orbital Studies of Titanium Nitride Chemical Vapor Deposition: Gas Phase $\beta$-Elimination. Chem. Phys. Lett. 2001, 340, 343–347.

(22) Umanhcki, S. Y.; Novoselov, K. P.; Minueshe, A. K.; Siddiqui, M.; Frenking, G.; Korkin, A. A. Thermodynamics and Kinetics of Initial Gas Phase Reactions in Chemical Vapor Deposition of Titanium Nitride. Theoretical Study of TiCl$_4$ Ammonolysis. J. Comput. Chem. 2001, 22, 1366–1376.

(23) Fowles, G. W. A.; Pollard, F. H. Studies on the Behaviour of Halides of the Transition Metals with Ammonia. Part II. The Reaction of Titanium Tetrachloride with Ammonia. J. Chem. Soc. 1953, 22, 2588.

(24) Kurtz, S. R.; Gordon, R. G. Chemical Vapor Deposition of Titanium Nitride at Low Temperatures. Thin Solid Films 1986, 140, 277–290.

(25) Nakamoto, K. Infrared Spectra of Inorganic and Coordination Compounds, 2nd ed.; John Wiley and Sons, Inc.: New York, 1970.

(26) Sosnov, E. A.; Malkov, A. A.; Malgyn, A. A. Chemical Transformations at the Silica Surface upon Sequential Interactions with Titanium Tetrachloride and Ammonia Vapors. Russ. J. Gen. Chem. 2015, 85, 2533–2540.

(27) Blomfield, G. A.; Little, L. H. Chemisorption of Ammonia on Silica. Can. J. Chem. 1973, 51, 1771–1781.

(28) Low, M. The Reaction of Ammonia with Si-O-SiHCl$_2$ Monolayers on Silica. J. Catal. 1981, 71, 144–151.

(29) Ohashi, M.; Yamanaka, S.; Hatton, J. M. Synthesis of $\beta$-ZnNCl by Thermal Decomposition of Zirconium(IV) Amide Trichloride. Bull. Chem. Soc. Jpn. 1986, 59, 2627–2628.

(30) Yamaguchi, S.; Miyaoaka, H.; Ichikawa, T.; Kojima, Y. Thermal Decomposition of Sodium Amide. Int. J. Hydrogen Energy 2017, 42, 5213–5219.

(31) Shamoto, S.; Iizawa, K.; Kato, T.; Yamada, M.; Yamanaka, S.; Ohoyama, K.; Ohashi, M.; Yamaguchi, Y.; Kajitani, T. Hydrogen in $\beta$-ZnNCl. J. Phys. Chem. Solids 1999, 60, 1511–1513.

(32) Mott, N. F. Conduction in Non-Crystalline Materials. Philos. Mag. 1969, 19, 835–852.

(33) Katoaka, N.; Terasima, K.; Tanaka, M.; Hosoda, W.; Taniguchi, T.; Wakita, T.; Muraoka, Y.; Yokoya, T. $\mu$-PEX Studies on TiNCl and Quasi-Two-Dimensional Superconductor Na-Intercalated TiNCl. J. Phys. Soc. Jpn. 2019, 88, 104709.

(34) Katoaka, N.; Tanaka, M.; Hosoda, W.; Taniguchi, T.; Fujimori, S.-I.; Wakita, T.; Muraoka, Y.; Yokoya, T. Soft X-Ray Irradiation Induced Metallization of Layered TiNCl. J. Phys. Condens. Matter 2022, 33, 035501.

(35) Jain, A.; Kumar, S.; Miyaoaka, H.; Zhang, T.; Isobe, S.; Ichikawa, T.; Kojima, Y. Ammonia Suppression during Decomposition of Sodium Amide by the Addition of Metal Hydride. Int. J. Hydrogen Energy 2017, 42, 22388–22394.