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Dissociative electron attachment to C_2N_2 molecules at surface and in gas phase

Z. W. Deng^{a)} and R. Souda^{b)}

Advanced Materials Laboratory, National Institute for Materials Science (AML/NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305, Japan

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We report an observation of strong emission of CN^- ions during heating of a nitrogen ion-irradiated graphite surface. An activation energy of $5.0\pm0.2 \text{ eV}$ for thermionic CN^- emission is derived from its temperature dependence. From the results of thermal desorption of neutral molecules and thermionic electron emission, it is proposed that the thermally induced CN^- ions may originate from the dissociative negative ionization of desorbing C_2N_2 molecules on the surface via a thermionic electron attachment mechanism. This mechanism is supported by the dissociative negative ionization of C_2N_2 molecules in the gas phase, as observed by negative ion RGA measurement. The large negative ionization cross section of C_2N_2 molecules at an electron energy of 0.8-0.9 eV, which also leads to the formation of CN^- ions, is believed to be responsible for the CN^- emission during heating of the nitrogen ion irradiated graphite. © 2002 American Institute of *Physics*. [DOI: 10.1063/1.1427705]

I. INTRODUCTION

Ion emission stimulated by electron, photon, ion, or thermal treatment is a subject of both physical and technical importance. Among these methods, the ionization that occurs on a hot surface, also referred to as surface ionization, produces ions with a narrow energy distribution and thus has the potential to act as an ion source for isotope analysis in ion mass spectroscopy. It is also of importance in tailoring particle-surface charge exchange mechanisms because it avoids the violent collision effect compared with the ionization induced by ion irradiation.

Studies on surface ionization date back to the early years of the past century.^{1–3} However, it is still a subject of scientific interest due to the lack of complete elucidation of the mechanisms,^{4–7} especially in case of surface negative ionization.^{8,9} Positive ionization usually occurs in alkali metals or alkali halides adsorbed on or remaining as residual impurities on high-work-function surfaces.^{1–3} The ionization mechanism is known to be related to the ionization potential of metals and the surface work function, and can be described by the Saha–Langmuir equation.¹⁰ Surface negative ionization is, however, still poorly understood despite extensive studies on many systems.^{8,9} Its efficiency was found to be much lower than that of positive ionization, and in many cases could not be described by the Saha–Langmuir equation.^{8,9}

More recently, there have been some studies on the surface ionization of either nonmetals or nonhalides, e.g., organic molecules.^{11–15} In a previous work,¹⁶ we reported an observation of strong thermionic emission of CN⁻ ions during heating of a nitrogen ion-irradiated graphite, and speculated a mechanism for this phenomenon according to its activation energy and the desorbed neutral species. In this work, we discuss this mechanism in greater detail with some additional lines of evidence, which include the surface work function of the nitrogen ion-irradiated graphite derived from the temperature dependence of the thermionic electron emission from the surface, the formation of CN^- ions during electron attachment to desorbed C_2N_2 molecules in the gas phase and its electron energy dependence observed with a newly available EPIC/IDP analyzer that can measure negative ions in the residual gas analysis (RGA) mode.

II. EXPERIMENT

This work was conducted on an UHV system with a base pressure of $< 1 \times 10^{-10}$ Torr, which is a combination of a mass-separated low-energy ion beam system with a HAL EQP/EQS analyzer (Hiden Analytical Ltd., England), as well as some other surface analysis instruments. The system has been described in detail elsewhere.¹⁷ The low-energy ion beam delivers a mass-separated ion beam with an energy of 5–800 eV used for nitrogen ion irradiation of graphite in this work.

Two mass analyzers were used for data acquisition. The HAL EQP/EQS analyzer consists of a high-transmission 45° sector field energy analyzer and a quadrupole mass spectrometer designed for secondary positive and negative ion mass spectrometry (SIMS) analysis. The configuration has been described elsewhere.¹⁷ Briefly, a field energy analyzer selects the energy of ions to be detected by scanning a filter voltage and the ion mass is analyzed by a rf quadrupole, yielding the energy and the mass distribution of the detected ions. An electron impact ionizer was also inserted into the analyzer head to function as a residual gas analyzer (RGA), making it possible to monitor the desorbed neutrals from the sample surface. In this mode, thermionic electrons emitted

^{a)}Corresponding author. Telephone: (81)-298-51-3354; fax: (81)-298-51-6280; electronic mail: DENG.Zongwu@nims.go.jp

^{b)}Electronic mail: SOUDA.Ryutaro@nims.go.jp

from a hot filament surface are accelerated to, e.g., 70 eV and then collide with the residual molecules, thereby leading to the ionization of the latter, during which the resultant positive ions are analyzed. By scanning the electron energy and recording the ion yield as a funciton of the electron impact energy, the electron energy threshold for the formation of a positive ion from a specific residual species (gas) could be determined by extrapolating the electron energy spectrum to a zero signal.¹⁸ The obtained electron energy thresholds help to clarify the origin of the specific positive ions, as discussed below.

For negative ion RGA measurement, another HAL EPIC/IDP analyzer was used. This analyzer is a quadrupole mass spectrometer designed for secondary positive and negative ion mass spectrometry analysis as well as positive and *negative* ion RGA measurement. It was used in this work for experiments on electron attachment to thermally desorbed C_2N_2 molecules in the gas phase, during which the negative ion yield was recorded as a function of the electron energy when scanning the electron energy. The obtained electron energy spectrum provided information on negative ionization via low-energy electron attachment and/or electron impact.

The sample holder used in this work was custom designed, which allowed resistive heating of the sample in UHV. A pyrolytic graphite sample was prepared by cleavage in air to a thickness of 0.2–0.3 mm and then held between two electrodes connected to two high-current feedthrough. The sample holder was supported by a turnable manipulator, allowing the sample surface to face either the ion beam or the analyzer. After mounting the sample holder into the chamber, the whole system was baked until a base pressure of $<1 \times 10^{-10}$ Torr was reached.

The sample was heated to 1200 °C in UHV for several cycles to clean the surface. After cooling down to room temperature (RT), it was irradiated by 800 eV N_2^+ ions with a dose of $1-1.5 \times 10^{18}$ ions/cm². Then, the sample was relocated in front of the EQP/EQS analyzer and *in situ* heated up to 1200 °C, during which the possible emission of positive and negative ions was monitored in the SIMS mode, and the desorption of neutrals was monitored in the (positive ion) RGA mode.

III. RESULTS AND DISCUSSION

For the sake of clarity, we first present results on the desorption of neutrals upon heating of the nitrogen ionirradiated graphite, which are important for the interpretation of the origin of CN^- ions. Figure 1 shows the positive ion RGA mass spectrum of desorbed neutral molecules obtained by the EQP/EQS analyzer in the positive RGA mode. The spectrum was accumulated during heating of the sample between 800 °C and 1200 °C. Two dominant neutral species, N₂(m/e 28) and C₂N₂(m/e 52), were identified, as well as small amounts of N(m/e 14), CN(m/e 26), and HCN(m/e 27). The neutral species that desorbed upon heating of the nitrogen ion irradiated graphite were monitored by other authors and assigned to N and CN radicals.¹⁹ The m/e 28 species were attributed to CO⁺ as a result of the reaction of hot graphite with residual oxygen in the UHV chamber. We are



FIG. 1. Positive ion RGA mass spectrum of thermally desorbed neutrals during heating of nitrogen ion-irradiated graphite.

uncertain why the authors failed to detect the m/e 52 species. However, we found that N_2 desorption would contribute much more than CO to the RGA signal at m/e 28 after careful treatment of the sample and monitoring of the desorbed species both before and after nitrogen ion irradiation.²⁰ The N and CN species of m/e 14 and 26, respectively, are mostly a consequence of the dissociative ionization of N_2 and C_2N_2 molecules, as demonstrated below.

The CN species may result from either direct desorption or dissociative ionization of C₂N₂ or both. This can be clarified by comparing the electron energy thresholds $(E_{\rm th})$ for the formation of CN⁺ and C₂N₂⁺ ions.¹⁸ Positive ion formation during RGA measurement involves ejection of a valence electron from its precursor molecule by electron impact. This process results in the formation of a parent ion, and sometimes also daughter ions as a result of bond breaking induced by the electron impact. For the formation of the parent ion, the electron energy threshold depends on the first ionization potential of the relevant precursor molecule. Accordingly, if CN⁺ originates from the direct ionization of the CN radical, its E_{th} should be close to that of $C_2N_2^+$ due to their very similar first ionization potentials (13.60 eV for CN and 13.37 eV for $C_2N_2^{(21)}$). The daughter ions should appear at higher electron energies than that of a parent ion because they require additional energy for bond breaking. As such, if CN⁺ is a result of the dissociative ionization of C_2N_2 , E_{th} of CN^+ should be several eV's higher than that of $C_2N_2^+$.²² If CN^+ originates from both channels, then we should observe two $E_{\rm th}$ values for CN⁺. Such an interpretation is also applicable to N^+ and N_2^+ .

Figure 2 shows the RGA CN^+ , $C_2N_2^+$, N^+ , and N_2^+ ion yields as a function of electron energy, yielding a higher E_{th} for the formation of CN^+ and N^+ than, respectively, that of $C_2N_2^+$ and N_2^+ . It is thus believed that most of the CN and N species may be produced by cracking of the C_2N_2 and N_2 molecules, respectively. In addition, the RGA yields of CN^+ and $C_2N_2^+$ showed an identical temperature dependence, in agreement with the above conclusion. Hence, the dominant thermally desorbed nitrogen-containing species from a nitrogen ion-irradiated graphite surface are ascribed to N_2 and C_2N_2 molecules, while the direct desorption of CN and N



FIG. 2. Incident electron energy scan for the formation of (a) CN^+ and $C_2N_2^+$ ions and (b) N^+ and N_2^+ ions in the positive ion RGA mode. The results show a higher electron energy threshold for the formation of CN^+ and N^+ than, respectively, that of $C_2N_2^+$ and N_2^+ , suggesting that most of the CN^+ and N^+ species in the positive ion RGA mass spectrum may be produced by cracking of the C_2N_2 and N_2 molecules.

radicals, if any, is very minimal and contributes much less than the cracking of C_2N_2 and N_2 molecules to the RGA yields of the CN and N species.

We now discuss the positive and negative ion emissions upon heating of the nitrogen ion-irradiated graphite. Figure 3 shows a SIMS spectrum of thermally desorbed negative species obtained with the analyzer working in the SIMS mode. The spectrum was also accumulated during heating of the



FIG. 3. A negative SIMS mass spectrum of thermally desorbed ions during heating of nitrogen ion-irradiated graphite.



FIG. 4. Temperature dependence of thermally desorbed CN^- and HCN^- ions from nitrogen ion-irradiated graphite, from which an activation energy of 5.0 ± 0.2 eV for negative ionization is derived. Note the parallel temperature dependence between CN^- and HCN^- emissions.

sample between 800 °C and 1200 °C. Significant emission of CN^- (m/e 26) ions was observed with a small amount of HCN^- (m/e 27, ~1% of CN^- yield) and a trace amount of H^- , sometimes F^- as well. No nitrogen- or carbon-containing positive species were detected in this process, but we indeed detected strong K^+ ion emission, which was found to have no correlation with the emission of CN^- ions.

The emission of negative ions exhibited a strong temperature dependence. Figure 4 shows a logarithmic plot of CN^- ion yield as a function of reciprocal temperature, from which an activation energy of 5.0 ± 0.2 eV for CN^- formation is derived. Also shown is a logarithmic plot of a HCN⁻ ion yield as a function of reciprocal temperature. The parallel temperature dependence suggests an identical activation energy for CN^- and HCN⁻ emissions. While the ions should originate from the ionization of some desorbed neutrals, this activation energy should be mainly attributed to the ionization process rather than the desorption process because the activation energy of neutral desorption was estimated below 1 eV.

Figure 5 shows the energy distribution spectrum of $CN^$ ions emitted during heating of the nitrogen ion-irradiated graphite, in which a double-peak structure is discernible despite the poor energy resolution of the analyzer, indicating the production of CN^- ions with different kinetic energies.

We exclude the possibility that the CN⁻ ions originate from the negative ionization of thermally desorbed CN radicals via tunneling of an electron from the surface to the desorbing CN radical. If this possibility were true, the activation energy for ionization would be related to the surface work function and the electron affinity of the CN radical. The surface work function of nitrogen ion-irradiated graphite can be estimated from thermionic electron emission, which is described by the Richardson equation, $J \propto A T^2 e^{-\phi/kT}$, where J is the saturation electron-current density emitted at absolute temperature T, ϕ is the surface work function, k is the Boltzmann constant, and A is a constant. Figure 6 shows the temperature dependence of thermionic electron emission plotted as ln (electron yield/T²) versus 1/T, from which the

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FIG. 5. Energy distribution of desorbed CN^- ions during heating of nitrogen ion-irradiated graphite. The double-peak structure indicates the production of CN^- ions with different kinetic energies.

surface work function of the nitrogen ion-irradiated graphite is derived to be \sim 4.06 eV. The electron affinity of the CN radical is \sim 3.82 eV,²³ yielding an activation energy of \sim 0.24 eV for CN⁻ emission. This value is far smaller than the obtained experimental value.

Another possibility is that the CN^- ion results from the attachment of a thermionic electron to a desorbing CN radical. However, its contribution to CN^- ions is limited to the very small desorption yield of CN radicals. On the other hand, when a free thermionic electron attaches to a CN radical, an excited temporary negative ion $(CN^-)^*$ is formed. The lifetime of this excited ion depends on whether the excess electronic energy (comprising the energy of the free electron plus the electron affinity of the CN radical) can be directly and effectively dispersed into its vibrational degrees of freedom. Otherwise, it would relax via autodetachment or via unimolecular decomposition into thermodynamically



FIG. 6. Temperature dependence of thermionic electron emission from a nitrogen ion-irradiated graphite surface, from which the surface work function is estimated to be \sim 4.06 eV.

stable fragments.²⁴ Considering the high electron affinity of the CN radical (3.82 eV), a very short lifetime and a very high autodetachment probability of the $(CN^-)^*$ ion are anticipated. The lifetime may be too short to allow detection of the $(CN^-)^*$ ions by the analyzer. Due to the above two limitations, this mechanism is not considered to be the dominant channel for CN^- ion emission, although it cannot be ruled out completely.

In the following discussion, we demonstrate that the dissociative negative ionization of the desorbed C_2N_2 molecules can also result in the formation of CN^- ions, which we believe is the major origin of the CN^- ions during heating of the nitrogen ion-irradiated graphite. The C_2N_2 molecule has the structure $N \equiv C - C \equiv N$ and is a pseudohalogen molecule due to the high electronegativity of the CN functional group. Cracking of the C-C bond leads to two CN particles. The mechanism is described as follows: In the course of the desorption of C_2N_2 molecules, a thermionic free electron attaches to a desorbing C_2N_2 molecule, leading to the formation of an excited transient negative ion $(C_2N_2^-)^*$. This is followed by dissociation in a very short time into a negative ion CN^- and a radical CN^* during decay:

$$C_2N_2(surface) + e^{-}(surface) \rightarrow (C_2N_2)^* \rightarrow CN^- + CN^{\bullet}$$

In this respect, we attribute the appearance of H⁻ and F⁻ ions to the dissociative negative ionization of the XY species (X, Y=H, F, CN). Dissociative electron attrachment to HCN molecules may also lead to the formation of CN⁻ ions. However, the C₂N₂ molecules are believed to be the major precursor of CN⁻ ions due to their much higher desorption yield. The absence of the C₂N₂⁻ ion indicates that the lifetime of the (C₂N₂⁻)* ion is too short to allow its detection as a parent ion.

The electron attachment process is believed to occur very near the surface because when a negative bias is applied to the sample, the energy distribution of CN⁻ ions exhibits a linear shift with unity ratio with the applied bias.¹⁶ It was also found that the desorption of the C2N2 molecules decayed rapidly with heating time at a fixed temperature, while the CN⁻ yield showed nearly no change with heating time when the C₂N₂ molecules were sufficiently accommodated.¹⁶ This, on one hand, is in agreement with a surface attachment mechanism because the gas-phase attachment will yield a synchronous decay of CN⁻ ions and C₂N₂ molecules. On the other hand, it suggests that the negative ionization may be governed by the thermionic electron emission process under such a condition, which then accounts for the identical activation energy for both CN^- and HCN^- emissions. If this were true, the activation energy for the formation of CN⁻ ions would be related only to the surface work function. In this respect, however, the obtained activation energy of CN⁻ emission is nearly 1 eV higher than the surface work function.

Evidence supporting the above mechanism comes from the formation of CN^- ions via the dissociative ionization of desorbed C_2N_2 molecules in the gas phase. For this purpose, another EPIC/IDP analyzer was used to measure negative ions in the RGA mode. After 800 eV, N_2^+ ion irradiation with a dose of $1-1.5 \times 10^{18}$ ions/cm², the sample was relocated in



FIG. 7. Electron energy dependence of CN^- ion formation (the relative negative ionization cross section) during electron attachment to thermally desorbed C_2N_2 molecules in the gas phase, measured by the EPIC/IDP analyzer in the negative ion RGA mode.

front of the analyzer, and resistively heated from RT up to 1200 °C, which led to the desorption of C2N2 and N2 molecules. The desorbed C2N2 molecules were ionized by very low-energy electrons emitted from the hot filament surface of the analyzer, resulting in the formation of CN⁻ ions. During heating, the sample was positively biased with a voltage of 10 V to suppress the thermionic emission of CN⁻ ions and electrons from the sample surface, which might otherwise affect the negative ion RGA measurement. Figure 7 shows the CN⁻ ion yield (the relative negative ionization cross section) as a function of electron energy. A strong peak appears at an electron energy of 0.8-0.9 eV, indicating a large negative ionization cross section at this energy. This peak is related to electron attachment to the desorbed C2N2 molecule (electron resonant transfer) to form a transient negative ion $(C_2N_2^-)^*$, which then dissociates into a CN⁻ ion and a CN[•] radical during decay. In addition, two other resonantlike contributions at electron energies of \sim 3.5 and 7.5 eV are discernible after enlarging the spectrum in the higher-energy range.

Figure 8 shows the negative ion RGA mass spectrum obtained at an electron energy of 0.9 eV. The spectrum was accumulated during heating of the nitrogen ion irradiated graphite from RT up to 1200 °C. The result shows dominant CN^- ions and no $C_2N_2^-$ ion, similar to the mass spectrum of the negative ions emitted directly from the hot sample surface (Fig. 3). The small but visible peaks at m/e 42 and sometimes at m/e 35 are attributed to N_3^- (Ref. 25) and Cl⁻, respectively.

We exclude the possibility that the CN^- ions originated from the dissociative adsorption of C_2N_2 molecules on the filament surface and the subsequent surface ionization of the desorbing CN radicals. The filament was set away from the trajectory of the incident molecules to prevent the surfaceionized species from entering the trajectory. In addition, the electron energy was gained by applying a negative bias to the filament. If the ions were formed on the surface, the kinetic energy of negative ions would increase with that of the elec-



FIG. 8. The negative ion mass spectrum during electron attachment to thermally desorbed C_2N_2 molecules in the gas phase, measured by the EPIC/IDP analyzer in the negative ion RGA mode. The incident electron energy was set at 0.9 eV.

trons. In this case, if the peak at an energy of 0.8-0.9 eV reflects the energy discrimination of the analyzer, there will be no reason for us to expect the two other peaks at energies of ~ 3.5 and 7.5 eV.

On the other hand, a study on low-energy electron attachment to the BrCN and ClCN molecules in the gas phase also showed the dominant formation of CN⁻ ions.²⁶ Due to the pseudohalogen characteristic of the CN functional group, the C₂N₂ molecules can be referred to as a pseudobihalogen molecule in analogy to BrCN and ClCN, making many of their chemical and physical characteristics comparable. In this respect, the electron energy dependence of CN⁻ formation during electron attachment to BrCN and CICN molecules showed a structure similar to that observed in the present work, i.e., a major peak appeared at electron energies of 0 eV (BrCN) and 0.5 eV (ClCN), accompanied by two additional resonantlike contributions at energies of ~ 1.8 and 5.5 eV in the case of BrCN, and at energies of \sim 1.6 and 6 eV in the case of ClCN.²⁶ We take the similar energy dependence spectrum of CN⁻ formation during very low-energy electron impact/attachment to BrCN, ClCN, and C2N2 as more evidence to support the interpretation of the results in Fig. 7. As such, the very low-energy electron attachment to C₂N₂ molecules did lead to the dissociative ionization of C₂N₂, resulting in the formation of CN⁻ ions. This is believed to be responsible for the thermionic CN⁻ emission during heating of the nitrogen ion-irradiated graphite.

The results in Fig. 7 also indicate that a kinetic energy of 0.8-0.9 eV is required for an electron to attach to the C_2N_2 molecule in order to reach the maximum of the negative ionization cross section. This value agrees well with and thus accounts for the activation energy difference between thermionic CN^- and electron emission.

The double-peak structure in the energy distribution spectrum as shown in Fig. 5 suggests emission of CN^- ions with different kinetic energies. These ions may originate from different precursor states of the transient negative ion $(C_2N_2^-)^*$. Because of the lack of knowledge on the electronic structure of the $C_2N_2^-$ ion, we cannot further assign the

 CN^- ion to the individual precursor states of $(C_2N_2^-)^*$. However, such a case was indeed observed during low-energy electron attachment to BrCN molecules, which showed the emission of Br⁻ ions with different kinetic energies by time-of-flight measurement and was attributed to two low-lying BrCN⁻ states, as predicted by *ab initio* calculations.²⁶ Although it was only observed in the case of BrCN and at higher electron energy, we speculate that such a case may occur during electron attachment to C_2N_2 molecules, even at lower energies, e.g., below 1 eV. This can be tested by the energy distribution of CN⁻ ions during electron attachment to C_2N_2 in the gas phase with an electron energy of below 1 eV. Unfortunately, to date our analyzers could not conduct such a measurement.

IV. CONCLUSION

Strong thermionic emission of CN⁻ ions was observed during heating of nitrogen ion-irradiated graphite. An activation energy of 5.0 ± 0.2 eV for CN⁻ emission is derived from its temperature dependence. Several possible mechanisms have been discussed to account for the origin of the CNions. The tunneling of an electron to a desorbing CN radical is ruled out in terms of the activation energy. The contribution of electron attachment to desorbing CN radicals is limited by the very small desorption of CN radicals and the lifetime of the resultant transient negative ions. It is then proposed that the thermionic CN⁻ emission may originate mainly from the dissociative negative ionization of desorbing C_2N_2 molecules on the surface by a thermionic electron attachment mechanism. This mechanism is supported by the formation of CN⁻ ions via low-energy electron attachment to desorbed C₂N₂ molecules in the gas phase. The large negative ionization cross section of C₂N₂ molecules at an electron energy of 0.8-0.9 eV, which also leads to the formation of CN⁻ ions, is believed to be responsible for the CN⁻ emission during heating of nitrogen ion-irradiated graphite. The observed electron energy at the maximum of the negative ionization cross section also agree with the activation energy difference between thermionic CN^- and electron emission.

- ¹M. J. Copley and T. E. Phipps, Phys. Rev. 45, 344 (1934).
- ²J. O. Hendricks, T. E. Phipps, and M. J. Copley, J. Chem. Phys. **5**, 868 (1937).
- ³S. Datz and E. H. Taylor, J. Chem. Phys. **25**, 389 (1956).
- ⁴M. D. Scheer and J. Fine, J. Chem. Phys. 46, 3998 (1967).
- ⁵L. Gladyszewski and G. Gladyszewski, Surf. Sci. 247, 274 (1991).
- ⁶T. Suzuki, H. Iwabuchi, K. Takahashi, M. Nomura, M. Okamoto, and Y. Fujii, Int. J. Mass Spectrom. Ion Processes **145**, 131 (1995).
- ⁷V. N. Ageev and S. Y. Davydov, Surf. Sci. **425**, 152 (1999).
- ⁸A. Persky, E. F. Greene, and A. Kuppermann, J. Chem. Phys. 49, 2347 (1968).
- ⁹J. C. Blais and G. Bolbach, Int. J. Mass Spectrom. Ion Processes **24**, 413 (1977).
- ¹⁰ I. Langmuir and K. H. Kingdon, Proc. R. Soc. London, Ser. A **107**, 67 (1925).
- ¹¹A. Danon and A. Amirav, J. Chem. Phys. 86, 4708 (1987).
- ¹²A. Danon and A. Amirav, J. Phys. Chem. **93**, 5549 (1989).
- ¹³H. Kishi and T. Fujii, J. Phys. Chem. **99**, 11153 (1995).
- ¹⁴H. Kishi and T. Fujii, J. Phys. Chem. 101, 3788 (1997).
- ¹⁵H. Kishi and T. Fujii, J. Chem. Phys. **108**, 1940 (1998).
- ¹⁶Z. W. Deng and R. Souda, Surf. Sci. **488**, 393 (2001).
- ¹⁷Z. W. Deng and R. Souda, Nucl. Instrum. Methods Phys. Res. B **183**, 260 (2001).
- ¹⁸I. Torres, R. Martínez, M. N. Sánchez Rayo, and F. Castaño, J. Phys. B 33, 3615 (2000).
- ¹⁹J. A. Taylor, G. M. Lancaster, and J. W. Rabalais, J. Am. Chem. Soc. **100**, 4441 (1978).
- $^{20}\mbox{Z}.$ W. Deng and R. Souda, Thin Solid Films (to be published).
- ²¹S. G. Lias, *CRC Handbook of Chemistry and Physics*, edited by D. R. Lide (CRC Press LLC, New York, 2000), pp. 10–178.
- ²²The bond dissociation energy of NC–CN should be ~4 eV or above in terms of the bond dissociation energies of Br–CN (~3.69 eV) and Cl–CN (~4.2 eV) (Ref. 26), and the π - π conjugation between the two CN functionals in the C₂N₂ molecule.
- ²³ T. M. Miller, in Ref. 21, pp. 10–147.
- ²⁴I. Hahndorf and E. Illenberger, Int. J. Mass Spectrom. Ion Processes 167/ 168, 87 (1997).
- ²⁵ M. Green, *Developments in Inorganic Nitrogen Chemistry*, edited by C. B. Colburn (Elsevier, Amsterdam, 1966), p. 39.
- ²⁶ F. Bruning, I. Hahndorf, A. Stamatovic, and E. Illenberger, J. Phys. Chem. 100, 19740 (1996).