PHYSICAL REVIEW A VOLUME 56, NUMBER 4 OCTOBER 1997

Formation of metastable N_2^- and CO^- anions in sputtering

Hubert Gnaser
Fachbereich Physik and Institut für Oberflächen- und Schichtanalytik, Universität Kaiserslautern, D-67663 Kaiserslautern, Germany

(Received 9 June 1997)

Sputtering the surface of a TiAlN(C,O) specimen with a 14.5-keV Cs^+ ion beam produces negative molecular ions of N_2^- and CO^-. They are detected in a double-focusing mass spectrometer operated at a mass resolution of $\sim 13\,000$; this provides a separation of interfering species in this mass region (e.g., Si^-, AlH^-) and a mass assignment at a precision of $\sim 10^{-4}$ amu. The flux of N_2^- relative to the stable N_3^- amounts to about 0.3. On average, one N_2^- is *formed* for 10^7 N atoms sputtered and a similar rate is observed for CO^-. The flight time through the mass spectrometer ($\sim 10\ \mu s$) sets a lower limit for the stability of these molecular anions. The abundant production of electronically excited molecules in sputtering is proposed to constitute the prerequisite for the formation of N_2^- and CO^-: these excited molecules may capture a surface electron forming thus a temporary negative-ion state (Feshbach resonance). By contrast, the upper limit for the emission of N^- is found to be less than one N^- per 10^{10} nitrogen atoms ejected, in agreement with the very short lifetimes of the excited N^- anions. [S1050-2947(97)50210-1]

PACS number(s): 34.50.Gb, 79.20.Rf, 33.15.Ta

Investigations into the formation of atomic and molecular negative ions have been a field of active research for many decades [1]. For most atomic ions electron affinities (EA's) are known rather precisely (e.g., with relative uncertainties as low as 5×10^{-7} for O and S) and are summarized in various compilations [2–5]. The situation is more complex for molecular ions: for many, not even their existence as negative ions has, as yet, been established. Among those, two have been investigated in this work: N_2^- and CO^-. The present study coincides with a brief mention as to the possible stability of N_2^- and CO^- in a recent publication [6] dealing with the formation of doubly charged negative carbon clusters. Already Massey [1] has put forward theoretical arguments against the stability of N_2^- and of the isoelectronic CO^-. The reasoning was that going from the N_2 closed-shell electron configuration to N_2^-, adding an additional electron in an antibonding $\pi_g 2p$ orbital, would reduce the binding energy by about 1.25 eV. Thus, the lowest level of N_2^- should be by this amount above that of N_2, and the vibrational levels of the N_2^- ground state would be unstable towards autodetachment. In a recent review [4] an EA value of -2.4 eV for both N_2^- and CO^- was quoted, but without specifying the origin of that datum. The formation of (short-lived) intermediate N_2^- states was inferred from resonances observed in electron scattering data (cf. Ref. [1]), but the level widths derived were indicative of a lifetime of the order of a vibration period. Experiments employing a two-step electron capture in alkali-metal-vapor targets [7] also appeared to show that N_2^- is not stable, although the data were considered to be not completely conclusive. The present work, therefore, attempts to establish sound evidence for the existence of N_2^- and CO^- anions.

There exists a variety of different means for producing and monitoring negative ions; they are discussed thoroughly in Refs. [1–5,8–10]. In the present work we utilize sputtering of a solid by an energetic 14.5-keV Cs^+-ion beam and analyze the ions formed by high-resolution mass spectrometry. It has been known for some time [11] that Cs^+ bombardment of solids (and the concurrent incorporation of cesium into the near-surface region) causes a prolific generation and emission of negative ions from that material. This finding is ascribed to a lowering of the sample's work function and the correlation between the work function, and the ionization probability of the sputtered ions can be described even in quantitative terms [12,13]. This kind of negative-ion production has two rather important applications for material characterization that provide additional stimulus for studying their formation. (1) In accelerator mass spectrometry [14] the sample to be analyzed is sputtered in a Cs-ion source to create negative ions, which then are accelerated (to MeV energies), converted to multiply-charged positive ions, accelerated again, and finally detected. An abundant beam of negative ions is, of course, of utmost importance. (2) The same holds for secondary-ion mass spectrometry [15], but as this technique provides the option for depth profiling and recording elemental-distribution images, the Cs^+-ion beam effecting sputtering can be focused to fairly small spot sizes ($\sim 1\ \mu$m, if desired). Detection of the ejected (negative) ions is carried out, e.g., in a double-focusing magnetic mass spectrometer. Using this technique, elemental concentrations in the range of 10^{12} atoms/cm^3 can be analyzed [16]. This is due to the very high ionization efficiency (close to 100% for elements with $A_e \geqslant 2$ eV) and the high instrumental transmission (10–20 %). The latter technique was employed in this work to search for metastable ions of N_2^- and CO^-.

The instrument is a standard secondary-ion mass spectrometer (Cameca IMS4f [17]). Primary Cs^+ ions are produced in a surface-ionization source, mass analyzed, and focused by electrostatic lenses. For the present experiments the beam current amounted to 0.2 μA and the beam size was $\sim 100\ \mu$m. It was raster-scanned across a surface area of $200\times200\ \mu m^2$ (current density ~ 0.5 mA/cm^2). The Cs^+ impact energy was 14.5 keV. The sample is at a potential of -4500 V and faces a grounded (extraction) electrode, which causes an acceleration of the emitted negative ions to an energy of 4.5 keV. The field strength in this region is 10 kV/cm. Upon passing the extraction electrode the

1050-2947/97/56(4)/2518(4)/$10.00

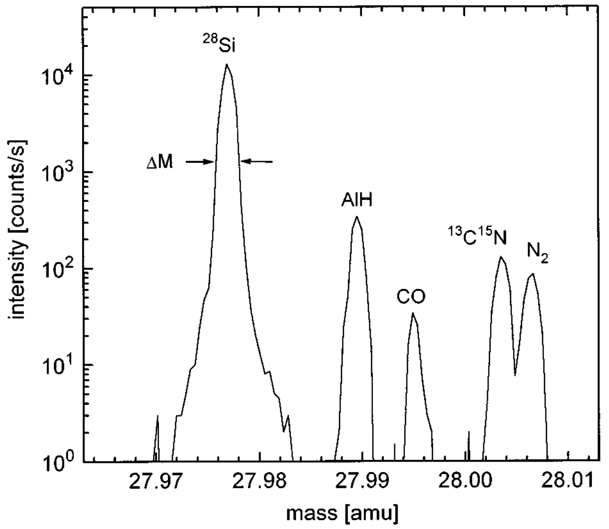

FIG. 1. High-resolution mass spectrum around 28 amu obtained by 14.5-keV Cs^+ sputtering of a TiAlN(C,O) specimen. The arrows at the ^{28}Si peak mark the width of the 10%-intensity level; the resulting value $\Delta M_{0.1} = 0.002\,17$ amu yields a mass resolution $M/\Delta M_{0.1} = 13\,000$.

negative-ion beam is focused by electrostatic lenses onto the entrance slit of the mass spectrometer proper. It consists of an electrostatic (spherical condenser) and a magnetic sector field both with a 90° deflection of the beam. Ions of the correct energy and mass-to-charge ratio pass the mass spectrometer exit slit. Between the sector fields an energy-selective slit is located that provides an energy resolution of $\Delta E \sim 10$ eV. The beam leaving the exit slit is refocused by a lens and, before being detected in a discrete-dynode electron multiplier, is subjected to another 90° deflection by an electrostatic sector whose dimensions are identical to the first one. Even with all slits fully open this triple deflection of the beam results in a negligible mass-*independent* background (<1 count in 10 s).

All of the present results were obtained at a fairly high mass resolution. This was accomplished by closing both the entrance and exit slits of the spectrometer. It will be shown below that a mass resolution of $M/\Delta M_{0.1} \sim 13\,000$ can be achieved thereby ($\Delta M_{0.1}$ corresponds to the width of a mass peak at 10% of its maximum intensity). The slit width is estimated to be 10 μm for these conditions. The pressure of residual gas both in the sample chamber and in the mass spectrometer was $\sim 1 \times 10^{-9}$ mbar.

The sample used in this study for the production of negative ions was a $Ti_{0.5}Al_{0.5}N$ film (4.5 μm thick) on a WC substrate. Independent analysis established that it also contained an appreciable amount of C and O (both partly replacing N) and that these elements exhibited a graded concentration throughout the film. This finding is of importance, as it provided another possibility of an unambiguous assignment of mass peaks to atomic and molecular species (e.g., high CO^- signal for high C and O concentrations in the film).

Figure 1 displays a high-resolution mass spectrum obtained in the 28-amu range. Five distinct peaks are observed in this 0.05-amu-wide mass region. Due to the hysteresis of the magnetic field an absolute calibration of the mass scale is possible only with an accuracy of ~ 0.01 amu. Nevertheless, a very clear peak assignment is possible by determining from the spectrum the differences between individual mass peaks. These mass differences (relative to the peak with the lowest mass in Fig. 1) were evaluated from several separate spectra recorded in this mass range and are compiled in Table I; they are compared there with the nominal values of the following ion species (in order of ascending mass): $^{28}Si^-$, AlH^-, CO^-, $^{13}C^{15}N^-$, and N_2^-. Both the excellent agreement of the numerical values and the fact that no other series of ion species that might occur in that mass range (e.g., $^{26}MgH_2$, $^{12}C^{15}NH$, BOH, ^{13}CNH) do fit the pattern observed in Fig. 1 (and in the other spectra recorded) indicate the correctness of the peak identification. Further evidence comes from the observation that the two other Si isotopes (at 29 and 30 amu) are observed at the correct isotopic abundances (Si is an impurity in this specimen with a concentration of about 10^{-4}). Furthermore, recording spectra at different depths in the film (which correspond to somewhat different C, N, and O content) causes the N_2^- and CO^- intensities to vary in correlation with the respective concentrations, while the Si^- and AlH^- signals stay unchanged.

TABLE I. Negative-ion species detected in the mass range around 28 amu (see Fig. 1) and their masses (column 2). Nominal mass differences Δ of the peaks relative to that of ^{28}Si (column 3) and the averaged values Δ_{expt} derived experimentally from several individual spectra (column 4). The numbers in parentheses give the statistical errors of the last two digits. All values are in amu.

Ion species	Mass	Δ	Δ_{expt}
^{28}Si	27.976 929		
AlH	27.989 364	0.012 44	0.012 38(13)
CO	27.994 915	0.017 99	0.017 89(10)
$^{13}C^{15}N$	28.003 462	0.026 53	0.026 58(21)
N_2	28.006 148	0.029 22	0.029 24(16)

In addition, the combination of energy and mass-to-charge selection virtually excludes interferences from fragmenting ion species. If such a process were to occur before the (first) electrostatic sector, the decay products would carry the wrong energy for being transmitted. Fragmentation between the electric and magnetic sector fields might produce ions of 28 amu, but with a magnetic rigidity (momentum-to-charge ratio) that does not match the magnetic field for 28-amu ions of the correct energy (4.5 keV). The final energy-dispersive element would also prevent such ion species from reaching the detector. The very precise mass assignment also makes such a fragmentation highly unlikely.

What cannot be excluded *a priori*, however, is the occurrence of doubly charged negative ions of twice the mass; for example, N_4^{2-} cannot be separated from N_2^-. On the other hand, $^{14}N_3{}^{15}N^{2-}$ is occurring at a half-integral mass number and could therefore be monitored at low mass resolution. The gain in sensitivity so obtained more than offsets the loss due to the lower abundance of this species as compared to $^{14}N_4$. No statistically significant signal, however, was detected, which rules out the possibility that doubly charged ions contribute to the signals of N_2^- and CO^-. This is not too surprising because the only doubly charged negative ions

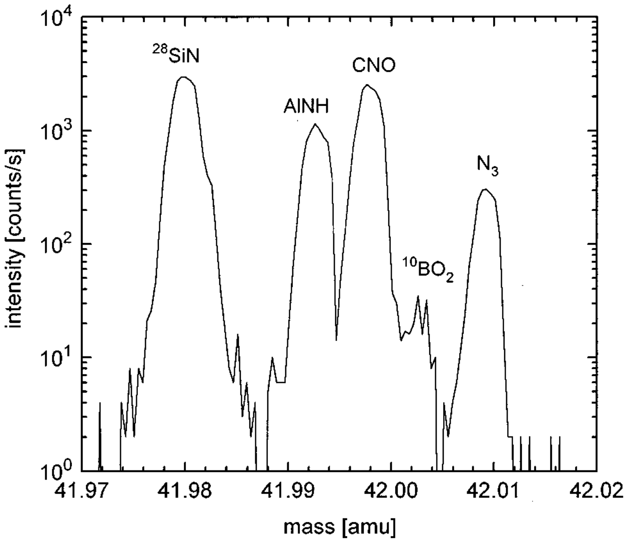

FIG. 2. High-resolution mass spectrum around 42 amu obtained by 14.5-keV Cs^+ sputtering of a TiAlN(C,O) specimen.

detected in sputtering so far [6,18,19] were C_n^{2-} cluster ions with $n \geqslant 7$ (one of those experiments [19] was carried out on the present instrument).

These observations provide convincing evidence that metastable N_2^- and CO^- ions are present in the sputtered flux. While the experimental setup is not suited to derive the lifetime of those ions, the flight time from the sample through the spectrometer ($\sim 10\ \mu s$) can be regarded as a lower limit of their stability.

Apart from the 28-amu region, other mass ranges were scrutinized in some detail. Figure 2 depicts a spectrum around 42 amu where abundant signals of N_3^- and CNO^- are observed. (The former ion has an EA of 2.70 eV [5].) From these data the N_2^-/N_3^- flux ratio is evaluated to be ~ 0.3, which is rather surprising in view of the fact that N_3^- is a stable ion while N_2^- is not believed to exist at all. At 44 amu mass peaks are observed that can be ascribed tentatively to N_2O^- and CO_2^-, albeit the intensities are rather low for an unambiguous identification and the former may interfere with $CN^{18}O$. Although CO_2^- is known [20] to form a metastable negative ion (with a lifetime of $\sim 90\ \mu s$), the low abundance in the present experiment is very probably due to the low concentration of oxygen in the specimen; thus the probability of forming a molecule carrying two O atoms is expected to be low. On the other hand, a distinct signal due to NO^- ions was observed.

We have investigated also the possible formation of N^-. This can be done by imposing less stringent conditions on the mass resolution: $M/\Delta M \sim 1700$ is sufficient to resolve N^- from $^{13}CH^-$ and $^{12}CH_2^-$. With the resulting mass-spectrometer transmission of about 1% (a factor-of-10 higher than for N_2^-), we were unable to detect a statistically significant signal at the N^- peak position. Thus, the upper limit for the formation under the present irradiation conditions was determined to be less than one N^- ion for 10^{10} N atoms sputtered. This is not too surprising in view of the recently computed [21] lifetime of the excited states of the nitrogen anion: for the ^3P state decaying by autoionization, a value of 3.8×10^{-14} s was determined, while for the ^1D and ^1S states, which can decay only via magnetic interactions, lifetimes of, respectively, 1.3×10^{-10} s and 7×10^{-11} s were reported [21].

Returning to the main topic of this work; that is, the detection of N_2^- and CO^- ions, the abundance of these species in the sputtered flux is of some interest. Comparing the signal strength of an abundant ion (e.g., CN^-) at low and at the presently employed high mass resolution, the transmission of the instrument for the latter conditions is estimated to amount to 10^{-3} (a factor-of-100 reduction). The sputtered flux of N atoms from the samples is about $10^{12}\ s^{-1}$. Taking the N_2^- count rate of $\sim 10^2$ ions/s (cf. Fig. 1) and the above-quoted transmission, we find that one N_2^- ion is formed on average for 10^7 N atoms sputtered from the surface. Although clearly a rare event, the detection and identification of these molecular ions are possible via the efficient mass spectrometry scheme employed.

One may assume that the metastable state of N_2^- (and, possibly, CO^-) is derived from an electronically excited neutral parent state relative to which it is bound (i.e., $A_e > 0$). In fact, available data on the emission of sputtered atoms and molecules show that they very often are emitted in electronically excited states [22]. Also rotational and vibrational excitation has been reported frequently [23]. Snowdon and Heiland [24] have investigated optical emission spectra of excited species in sputtering of nitrogen and carbon-oxygen implanted silicon. Specifically, they report the identification of either or both the $N_2\ B\,^3\Pi_g$ and $N_2^+\ A\,^2\Pi_u$ states. The first gives rise via the $N_2\ B\,^3\Pi_g$–$A\,^3\Sigma_u^+$ transition (first positive system) to emission features that imply the population of high vibrational states ($v' = 6-12$). They ascribe [24] these observations to the Lewis-Rayleigh afterglow proceeding via the recombination of two $N(^4S^0)$ atoms: $N(^4S^0) + N(^4S^0) \leftrightarrow N_2\ ^5\Sigma_g^+$, followed by the stabilization $N_2\ ^5\Sigma_g^+ + \text{surface} \rightarrow N_2\ B\,^3\Pi_g + \text{surface}$, where the surface acts as third body. Such a process would be indicative of an association mechanism in the sputtering event that can produce the observed vibrational and broad rotational level populations. Others authors [25] observed a strong emission only from the $N_2\ C\,^3\Pi_u$–$B\,^3\Pi_g$ bands. The sputtering conditions employed would favor an ejection in a single-collision event, that is, by a recoil from an individual atom at the surface, which especially is applicable to molecules with strong bonding and equal (or similar) masses [26,27]. Both of these conditions fit N_2^- and CO^-. The situation was less clear-cut in the case of CO. Here the CO $C\,^1\Sigma$–$A\,^1\Pi$ and/or CO^+ $B\,^2\Sigma$–$A\,^2\Pi$ transitions were tentatively identified [24].

In view of those results there is good reason for the assumption that a considerable fraction of N_2 and CO is in an excited state upon leaving the solid, which might constitute the precursor for the negative ions. A possible process might be as follows. At the rather low work function of the surface (due to cesium incorporation), these excited molecules may capture an electron, thus forming a temporary negative-ion state (Feshbach resonance). A similar mechanism was proposed [28] to explain electron emission observed in slow collisions of N_2^+ with cesiated low-work-function surfaces, as resulting from autodetachment of the resonance state N_2^{-*} $E\ ^2\Sigma_g^+$, which was created by electron transfer to the projectile neutralized before into a Rydberg state. As the lifetime of such states is, very probably, not compatible with the flight time of N_2^- ions observed in the present experiment (about 10 μs), metastable quartet states of N_2^- and CO^- might be invoked to explain their rather long lifetimes.

In summary, the present study provides unambiguous evidence for the production of negative N_2^- and CO^- ions in sputtering at keV energies. Earlier observations [23–25] of an abundant emission of excited N_2 and CO molecules suggest that these excited states are a necessary condition for the formation of N_2^- and CO^-. Future investigations might, therefore, try to correlate those findings, employing a suitable experimental setup. Apart from their mere existence, the ions' flight time in the mass spectrometer ($\sim$10 μs) establishes some boundary with respect to their lifetime. It is also noted that the ions experience an electric field of 10 kV/cm in the initial acceleration; in view of the (relatively) abundant fluxes of N_2^- and CO^- this field is apparently too weak for an efficient electron detachment. Thus, future studies might be devised to utilize electron detachment in a varying electric field as a means for the determination of the binding energies of N_2^- and CO^- anions.

The author is grateful to H. Hotop for very stimulating and helpful conversations and to H. Oechsner for his support of this work.

[1] H. S. W. Massey, *Negative Ions* (Cambridge University Press, Cambridge, England, 1976).

[2] H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **4**, 539 (1975); **14**, 731 (1985).

[3] B. K. Janousek and J. I. Brauman, in *Gas Phase Ion Chemistry Vol. 2*, edited by M. T. Bowers (Academic, New York, 1979), p. 53; P. S. Drzaic, J. Marks, and J. I. Brauman, in *Gas Phase Ion Chemistry Vol. 3*, edited by M. T. Bowers (Academic, New York, 1984), p. 167.

[4] M. K. Scheller, R. N. Compton, and L. S. Cederbaum, Science **270**, 1160 (1995).

[5] D. R. Bates, Adv. At. Mol. Phys. **27**, 1 (1991).

[6] R. Middleton and J. Klein, Nucl. Instrum. Methods Phys. Res. B **123**, 532 (1997).

[7] Y. K. Bae, M. J. Coggiola, and J. R. Peterson, Phys. Rev. A **29**, 2888 (1984).

[8] S. J. Buckman and C. W. Clark, Rev. Mod. Phys. **66**, 539 (1994).

[9] C. Desfrançois, H. Abdoul-Carime, and J.-P. Schermann, Int. J. Mod. Phys. B **10**, 1339 (1996).

[10] T. Andersen, Nucl. Instrum. Methods Phys. Res. B **123**, 508 (1997).

[11] V. E. Krohn, J. Appl. Phys. **33**, 3523 (1962).

[12] M. L. Yu and N. D. Lang, Phys. Rev. Lett. **50**, 127 (1983).

[13] H. Gnaser, Phys. Rev. B **54**, 16456 (1996).

[14] A. E. Litherland, Annu. Rev. Nucl. Part. Sci. **30**, 437 (1980).

[15] A. Benninghoven, F. G. Rüdenauer, and H. W. Werner, *Secondary Ion Mass Spectrometry* (Wiley, New York, 1987).

[16] H. Gnaser, Surf. Interface Anal. (to be published).

[17] H. N. Migeon, C. Le Pipec, and J. J. Le Goux, in *Secondary Ion Mass Spectrometry SIMS V*, edited by A. Benninghoven R. J. Colton, D. S. Simons, and H. W. Werner (Springer, Berlin, 1986), p. 155.

[18] S. N. Schauer, P. Williams, and R. N. Compton, Phys. Rev. Lett. **65**, 625 (1990).

[19] H. Gnaser and H. Oechsner, Nucl. Instrum. Methods Phys. Res. B **82**, 518 (1993).

[20] R. N. Compton, P. W. Reinhardt, and C. D. Cooper, J. Chem. Phys. **63**, 3821 (1975).

[21] R. D. Cowan, C. Froese Fischer, J. E. Hansen, and V. Kempter, J. Phys. B **30**, 1457 (1997).

[22] M. L. Yu, in *Sputtering by Particle Bombardment III*, edited by R. Behrisch and K. Wittmaack (Springer, Berlin, 1991), p. 91.

[23] E. W. Thomas, Prog. Surf. Sci. **10**, 383 (1980).

[24] K. J. Snowdon and W. Heiland, Z. Phys. A **318**, 275 (1984).

[25] E. W. Thomas and L. Efstathiou, Nucl. Instrum. Methods Phys. Res. B **2**, 479 (1984).

[26] H. Oechsner, in *The Physics of Ionized Gases*, edited by M. M. Popovic and P. Krstic (World Scientific, Singapore, 1985), p. 571.

[27] H. M. Urbassek, Nucl. Instrum. Methods Phys. Res. B **18**, 587 (1987).

[28] H. Müller, R. Hausmann, H. Brenten, and V. Kempter, Surf. Sci. **303**, 56 (1994).