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Experimental and theoretical investigations of the structure and the stability of the BNSi molecule

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Theoretical computations were carried out to determine the structure and molecular parameters of the BNSi molecule. The most stable isomer is found to have a BNSi linear geometry. Thermal functions as derived from the theoretical computed molecular parameters were used in the evaluation of the thermodynamic properties of BNSi from high-temperature Knudsen effusion mass spectrometric equilibrium data. From the reactions analyzed by the second-law and third-law methods, the enthalpy of formation, $\Delta_f H_0^o$, and of atomization, $\Delta_a H_0^o$, in kJ mol^{-1}, for BNSi, were obtained as 398 ± 16 and 1078 ± 17, respectively. © *1999 American Institute of Physics.* [S0021-9606(99)30942-9]

I. INTRODUCTION

The great impulse motivated by research on new materials for electronic devices, has lead to a large number of studies to develop and better characterize these new materials.[1–3] Especially thin films containing silicon, boron, and nitrogen find a variety of applications, for instance, as low dielectric constant materials for the reduction of the parasitic capacitance in order to improve the overall performance of large scale integrated circuits (LSI).[4,5] Furthermore the incorporation of silicon atoms in boron nitride films produces an improvement in the properties and stability of the films.[6] It has also been found that amorphous Si–N–B films obtained by plasma-enhanced chemical vapor deposition (CVD) present good insulation characteristics and conformal step coverage.[6] Finally, this ternary material has also been used as a good chemical/mechanical polish by Neureither *et al.*[7]

Apart from providing insight into the nature of bonding of these species, equilibrium vaporization studies contribute to the understanding of the formation of thin solid films containing these elements.

No experimental data or theoretical studies on the BNSi molecule have been reported in literature. In the present investigation we report the first experimental data based on equilibrium measurements employing Knudsen cell mass spectrometry and the first theoretical computation of the BNSi molecule. This work is in continuation of our mass spectrometric equilibrium investigations of small semiconductor nitride clusters.[8,9]

Our computed values for the enthalpy of atomization, $\Delta_a H_0^o$, and appearance potential are compared with our corresponding experimental values. Preliminary experimental results have been reported elsewhere.[10]

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II. THEORETICAL INVESTIGATIONS

Ab initio calculations were carried out utilizing the GAUSSIAN 98 program package[11] in order to obtain the molecular parameters of the BNSi ground state. The results have been used to calculate the thermal functions for BNSi needed in the evaluation of the mass spectrometric equilibrium data to obtain its thermodynamic properties.

The calculations were performed at five levels of theory: (i) the density functional (DF) method using the Becke three-parameter exchange functional with the Lee, Yang, and Parr correlation functional (B3LYP), (ii) the Hartree–Fock approach (HF), (iii) the second-order Møller–Plesset perturbation theory (MP2), (iv) the coupled-cluster method (CCD), and (v) the coupled cluster singles and doubles excitations approach including the effect of connected triples excitations [CCSD(T)]. They were applied using a triple-zeta polarized and diffuse basis set, 6-311+G*, as well as correlated consistent polarized valence double-zeta, cc-pVDZ, and triple-zeta basis sets, cc-PVTZ.

Among the four possible connectivities for the molecule with boron–nitrogen–silicon stoichiometry, three acyclic structures, BNSi, BSiN, SiBN, and a cyclic one, respectively, were considered. In order to compare the stability of the various isomers, the relative energies were computed at the CCSD(T)/cc-pVTZ level of theory but with the optimized geometry obtained at the MP2/cc-pVTZ level. This is justified because for the BNSi calculations there were no large differences between the optimized geometry at the MP2 and CCSD(T) level of theory (see Table I). From the calculations the most stable configuration is found to have a linear geometry with nitrogen located between boron and silicon. This result is also in agreement with experimental and theoretical results for the similar molecules, Si$_2$N (Refs. 12, 13) and B$_2$N (Refs. 14–16), which too have linear structures as the most stable geometry, with nitrogen in the center.

The cyclic structure is optimized to linear with the BNSi

TABLE I. The optimized molecular parameters and the energy of the $^1\Sigma^+$ ground state of linear BNSi at different levels of theory.

Method	Basis set	Total energy[a]	r_{B-N}[b]	r_{N-Si}	ν_1[c]	ν_2	ν_3
B3LYP	6-311+G*	−369.066 9090	1.372	1.589	1554	851	121
	cc-pVDZ	−369.039 0056	1.383	1.603	1533	835	112
	cc-pVTZ	−369.077 4413	1.368	1.587	1565	855	97
HF	6-311+G*	−368.030 1334	1.364	1.559	1654	931	176
	cc-pVDZ	−368.006 7503	1.372	1.572	1636	916	153
	cc-pVTZ	−368.045 2175	1.359	1.558	1667	934	152
MP2	6-311+G*	−368.333 7292	1.384	1.596	1529	831	78
	cc-pVDZ	−368.298 4106	1.399	1.614	1502	803	103
	cc-pVTZ	−368.397 3679	1.382	1.595	1543	831	92
CCD	6-311+G*	−368.352 9697	1.382	1.580	1570	872	121
	cc-pVDZ	−368.319 4632	1.395	1.597	1540	849	118
	cc-pVTZ	−368.413 8319	1.378	1.578	1582	875	115
CCSD(T)	6-311+G*	−368.374 2712	1.388	1.592	1530	838	94
	cc-pVDZ	−368.339 3236	1.402	1.612	1493	809	95
	cc-pVTZ	−368.439 0062	1.385	1.591	1540	840	89

[a]The computed total energy in hartree.
[b]The bond lengths are in Å.
[c]ν_1 is the B–N stretching, ν_2 the Si–N stretching, and ν_3 the bending vibrational mode, in cm^{-1}.

structure; the SiBN and BSiN geometries are linear, and are 181 and 458 kJ mol^{-1}, respectively, higher in energy than the most stable BNSi isomer.

A $^1\Sigma^+$ state is calculated as the electronic ground state for BNSi.

The vibrational frequencies for the three vibrational normal modes of B–NSi stretching, ν_1, Si–NB stretching, ν_2, and B–N–Si bending vibrations, ν_3, in the $X\,^1\Sigma^+$ state were calculated at all levels of theory used and are listed in Table I. The computed energy and the molecular parameters for the ground state of BNSi optimized at different levels of theory are also given in Table I.

At the highest level of theory, CCSD(T)/cc-pVTZ, the geometrical parameters of BNSi, show a boron–nitrogen bond distance equal to 1.385 Å and a silicon–nitrogen bond distance equal to 1.591 Å. The B–N internuclear distance is very close to that of 1.403 Å in H_2BNH_2,[17] which has a double bond character, and slightly longer than the triple bond of 1.335 Å (Ref. 18) of the BN molecule, derived from the rotational constant of its ground state. The Si–N internuclear distance is very close to that of the double bond of 1.576 Å in H_2SiNH,[19] calculated at the $HF/6\text{-}31G^{**}$ level of theory.

From Table I, it is noted that there is no pronounced trend of the internuclear distances with the level of *ab initio* treatment. For the vibrational frequencies, there is a slight difference in the values from the HF calculations and the correlated calculations. At the HF/cc-pVTZ level the values for the ν_1 and ν_2 stretching modes are about 10% higher than those obtained at the CCSD(T)/cc-pVTZ level. The ν_3 bending frequency at the HF/cc-pVTZ level is about 70% higher than that calculated at the CCSD(T)/cc-pVTZ level.

In the evaluation of the thermal functions of BNSi we used our computed values obtained at the highest level of theory, CCSD(T)/cc-pVTZ. Table II lists the thermal functions calculated for BNSi. In order to support our choice for the molecular parameters of BNSi, we calculated the bond distances and the vibrational frequencies for the AlNC molecule, isoelectronic with BNSi, at the same level of theory, CCSD(T)/cc-pVTZ. The results are reported in Table III. The agreement between the experimental values and our computed parameters is very good.

III. MASS SPECTROMETRIC MEASUREMENTS

All equilibrium measurements were done with a Nuclide Corporation mass spectrometer. The technique and the experimental procedure have been described elsewhere.[20]

TABLE II. The Gibbs energy functions, $(G_T^o - H_0^o)/T$ (GEF$_0$), in JK^{-1} mol^{-1}, and the heat content functions, $H_T^0 - H_0^o$ (HCF$_0$) in kJ mol^{-1}, for the BNSi molecule.

	Temperature (K)					
	298.15	1400	1600	1800	2000	2000
−GEF$_0$	211.8	286.2	293.4	299.9	305.7	311.1
HCF$_0$	12.83	75.06	87.17	99.36	111.6	123.9

TABLE III. Comparison between our calculations and the experimental molecular parameters of the AlNC molecule.

Method	r_{Al-N}[a]	r_{N-C}	ν_1[b]	ν_2	ν_3
CCSD(T)/cc-pVTZ	1.868	1.188	2065	553	103
MWS[c]	1.849	1.171			
LEFS[d]			2069	549	100

[a]The bond lengths are in Å.
[b]ν_1 is the C–N stretching, ν_2 the Al–N stretching, and ν_3 the bending vibrational mode, in cm^{-1}.
[c]MWS is for millimeter-wave spectrum, see Ref. 31.
[d]LFES is for laser fluorescence excitation spectra, see Ref. 32.

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TABLE IV. Measured ion currents, in A, over Si_3N_4+Si system in BN, and third-law values, in kJ mol^{-1}, of the $\Delta_r H_0^o$ for reaction (1) and reaction (2).

| T (K) | Ion intensities | | | | | $\Delta_r H_0^o$ reaction (1) | $\Delta_r H_0^o$ reaction (2) |
	Si^+	Si_2^+	Si_2N^{+a}	B^+	$BNSi^{+a}$		
Series 1							
1834	$3.1E-10$	$8.0E-12$	$8.4E-12$	$5.4E-14$	$9.9E-13$	-72.9	653.7
1798	$2.0E-10$	$5.0E-12$	$5.5E-12$	$3.5E-14$	$4.9E-13$	-67.2	652.7
1834	$2.8E-10$	$7.0E-12$	$9.4E-12$	$6.2E-14$	$9.3E-13$	-66.6	654.7
1856	$3.6E-10$	$9.6E-12$	$1.2E-11$	$6.3E-14$	$1.5E-12$	-74.7	654.4
1874	$4.7E-10$	$1.3E-11$	$1.5E-11$	$8.0E-14$	$2.0E-12$	-76.9	655.6
1897	$6.0E-10$	$1.8E-11$	$2.7E-11$	$1.3E-13$	$2.7E-12$	-69.5	658.0
1868	$5.3E-10$	$1.4E-11$	$1.9E-11$	$1.1E-13$	$2.2E-12$	-71.3	652.2
					Average	-71.3 ± 3.8	654.5 ± 1.9
Series 2							
1898	$2.6E-10$	$7.6E-12$	$8.0E-12$	$4.9E-14$	$1.0E-12$	-75.3	657.2
1959	$4.9E-10$	$1.5E-11$	$2.2E-11$	$1.0E-13$	$2.0E-12$	-71.3	664.7
2000	$7.3E-10$	$2.4E-11$	$3.3E-11$	$2.1E-13$	$3.8E-12$	-71.1	666.5
2061	$1.8E-09$	$7.6E-11$	$9.1E-11$	$5.1E-13$	$1.2E-11$	-75.9	664.8
2015	$7.2E-10$	$2.1E-11$	$2.5E-11$	$3.4E-13$	$4.5E-12$	-70.8	668.1
2026	$8.3E-10$	$2.4E-11$	$2.8E-11$	$4.3E-13$	$5.3E-12$	-70.5	668.6
2052	$9.2E-10$	$2.8E-11$	$2.7E-11$	$8.2E-13$	$6.6E-12$	-66.5	675.4
2001	$6.5E-10$	$1.5E-11$		$5.1E-13$	$4.2E-12$		665.1
2009	$6.3E-10$	$1.8E-11$	$1.2E-11$	$5.7E-13$	$3.6E-12$	-68.3	670.0
1975	$4.4E-10$	$1.4E-11$	$9.7E-12$	$2.7E-13$	$2.1E-12$	-68.1	668.8
1947	$3.5E-10$	$8.9E-12$	$5.8E-12$	$1.7E-13$	$1.5E-12$	-73.7	665.7
1931	$3.1E-10$	$6.9E-12$	$5.1E-12$	$1.5E-13$	$1.2E-12$	-71.6	664.4
1915	$2.4E-10$	$5.5E-12$	$3.5E-12$	$1.2E-13$	$8.0E-13$	-70.0	666.0
1902	$2.1E-10$	$4.8E-12$	$3.1E-12$	$9.8E-14$	$7.1E-13$	-70.7	663.8
1894	$1.8E-10$	$4.0E-12$	$2.5E-12$	$7.0E-14$	$5.7E-13$	-73.1	664.8
1882	$1.5E-10$	$3.4E-12$	$2.2E-12$	$7.2E-14$	$4.5E-13$	-67.7	664.7
1870	$1.2E-10$	$2.8E-12$	$1.6E-12$	$4.8E-14$	$3.4E-13$	-70.7	665.2
1846	$8.1E-11$	$1.8E-12$	$1.1E-12$	$2.4E-14$	$1.9E-13$	-71.1	666.5
					Average	-71.0 ± 2.5	666.0 ± 3.2

^{a}Ion intensities have been corrected for small contributions of Si_2C and SiC_2 (see text).

The BNSi molecule had first been identified in connection with the investigation of the Si_5 cluster[21] but its evaluation was obscured by the presence of gaseous silicon carbides.[9,22]

The sample, a mixture of semiconductor grade silicon powder, and Si_3N_4 of 99.9% purity, was evaporated from a boron nitride Knudsen cell with an orifice diameter of 1.0 mm, placed inside a graphite cell having a molybdenum lid. The molybdenum lid, instead of the graphite lid,[9] was used to minimize the formation of silicon carbides, SiC_2 and Si_2C, and the overlap of their isotopes with those of BNSi and Si_2N, respectively. The cell was heated by radiation by a tungsten coil resistor and the temperatures were measured by a calibrated optical pyrometer focused onto a black body hole at the bottom of the graphite cell. Appropriate window and prism corrections were applied. The energy of the ionizing electron was 12.5 eV, the emission current 10 mA, the ion-accelerating voltage was 4.5 kV, and the electron multiplier was operated at -3 kV.

The ions pertinent to the present investigation, namely B^+, Si^+, Si_2^+, Si_2N^+, $BNSi^+$, SiC_2^+, and Si_2C^+ were identified by their mass to charge ratio, isotopic abundance, shutter effect, and ionization efficiency curves. The electron impact energy scale was calibrated with B (8.296 eV) (Ref. 23) and Si (8.149 eV).[23] The appearance potential of 8.2 ±0.5 eV, was derived for $BNSi^+$ by the linear extrapolation method. This value is in good agreement with that of 7.98 eV, calculated at the CCSD(T)/cc-pVTZ level of theory.

The pressure calibration constants were determined from the known $Si_2(g)=2$ $Si(g)$ dissociation reaction, in the same way as described elsewhere.[9] The resulting values, of k_i, in atm A^{-1} K^{-1}, are for series 1 and 2: Si, 8.11 and 23.6; Si_2, 5.86 and 17.0; B, 33.5 and 97.6; Si_2N, 5.39 and 15.7; BNSi, 9.61 and 28.0.

Table IV lists the measured ion currents for the most abundant isotopes of the species pertinent to the present investigation. Each of the ion intensities of Si_2N^+ and $BNSi^+$ has been corrected for small contributions due to Si_2C and SiC_2, respectively. For $BNSi^+$ the maximum correction from SiC_2, at $m/e=53$, was 2%, and for Si_2N^+ it was 10% from Si_2C, at $m/e=70$.

IV. RESULTS AND DISCUSSION

The Gibbs energy functions, $(G_T^o-H_0^o)/T$(GEF$_0$), and the heat content functions, $H_T^o-H_0^o$(HCF$_0$), needed in the evaluation of the reaction enthalpies were taken from literature for B(g),[24] Si(g),[25] Si(cond.),[25] BN(s),[26] $Si_2(g)$,[27] and $Si_2N(g)$.[9] Those for BNSi(g) were calculated according to statistical thermodynamic procedures, using the rigid-rotator harmonic-oscillator approximation.[28]

TABLE V. Summary of the enthalpies of reaction, in kJ mol^{-1}, for the two series of experiments.

Reaction	Second-law		Third-law	$\Delta_r H_0^o$ selected
	$\Delta_r H_{\langle T \rangle}^o$	$\Delta_r H_0^o$	$\Delta_r H_0^o$	
Series 1				
$Si_2N(g) + B(g) = BNSi(g) + Si(g)$	$\cdots$	$\cdots$	-71.3 ± 3.8^a	-71.3 ± 3.8
$BN(s) + Si(cond.) = BNSi(g)$	$\cdots$	$\cdots$	654.5 ± 1.9	654.5 ± 1.9
Series 2				
$Si_2N(g) + B(g) = BNSi(g) + Si(g)$	-81.3 ± 18.4	-78.1 ± 18.4	-71.0 ± 2.5	-73.4 ± 6.2
$BN(s) + Si(cond.) = BNSi(g)$	561.5 ± 19.4	622.6 ± 19.4	666.0 ± 3.2	651.5 ± 6.6

[a]The error terms are standard deviations.

For the determination of the enthalpy of formation, $\Delta_f H_0^o$, and the atomization enthalpy, $\Delta_a H_0^o$, of the BNSi molecule, the enthalpy changes for the reactions:

$$Si_2N(g) + B(g) = BNSi(g) + Si(g), \qquad (1)$$

$$BN(s) + Si(cond) = BNSi(g), \qquad (2)$$
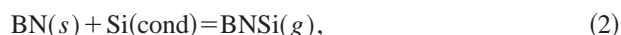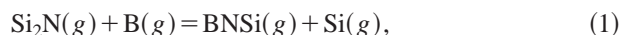
were evaluated according to the second-law method, based on a least-squares analysis of $\ln K_p$ vs. $1/T$ plots, and according to the third-law method, using the relation $\Delta_r H_0^o = -RT \ln K_p - T\Delta[(G_T^o - H_0^o)/T]$.

Reaction (1) is an all gas phase pressure independent reaction, and reaction (2) is pressure dependent. Table V lists the results of the second-law and third-law evaluations. For series 2 the selected value of $\Delta_r H_0^o$ for each reaction was obtained by giving the third-law value twice the weight of the second-law value; whereas for series 1 only a third-law analysis was used because of too few data points.

The necessary enthalpies of formation, $\Delta_f H_0^o$, in kJ mol^{-1}, used to obtain the final values for the enthalpy of formation and atomization of BNSi were: 560 ± 5,[24] 470.82 ± 0.10,[26] 445.7 ± 4.0,[25] -247.99 ± 1.55,[26] for B(g), N(g), Si(g), and BN(s), respectively. The atomization enthalpy of $Si_2N(g)$, $\Delta_a H_0^o$, in kJ mol^{-1}, used was 1011.2 ± 12.4.[9]

From the selected $\Delta_r H_0^o$ values (see Table V) and these auxiliary literature data, the respective $\Delta_f H_0^o$ and $\Delta_a H_0^o$ values were derived for each reaction. By giving the same weight to the reactions (1) and (2), we obtain for the $\Delta_f H_0^o(BNSi, g)$, $\Delta_f H_{298.15}^o(BNSi, g)$, $\Delta_a H_0^o(BNSi, g)$, and $\Delta_a H_{298.15}^o(BNSi, g)$, in kJ mol^{-1}, the values 398.4 ± 16, 402.3 ± 16, 1078.2 ± 17, and 1085.4 ± 17, respectively. Here the overall uncertainties were determined as described elsewhere.[29] Our computed $\Delta_a H_0^o(BNSi, g)$ of 1017 kJ mol^{-1} is about 6% smaller than the experimental value, obtained in the present investigation.

It is interesting to compare the thermodynamic stabilities of similar molecules. Atomization enthalpies, $\Delta_a H_0^o$, in kJ mol^{-1}, of the molecules Si_2B,[30] Si_2N,[9] B_2N,[10] and BNSi are: 767 ± 18, 1011 ± 12, 1068 ± 25, and 1078 ± 17, respectively. As can be seen, the thermodynamic stability increases from Si_2B to BNSi; in particular, BNSi is more stable than Si_2N and B_2N by 67 and 10 kJ mol^{-1}, respectively.

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