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Interactions of hydride species and their roles in carbon nitride growth

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The relative reactivity among neutral radicals, cations, and anions of various carbon and nitrogen hydride species, as well as the reactivity of these species with substrates of pseudocubic- and β-phase carbon nitrides, have been studied by analyzing their frontier orbitals calculated at Hartree–Fock and configuration interaction levels of theory using 6-31G** and 6-31++G** basis sets. For small species, the relative reactivity obtained in this study agrees well with the trend deduced from the available experimental rate constants. Our results show that both neutral carbon hydrides and nitrogen hydrides are less reactive than their cations and anions with the surfaces of carbon nitride substrates, and the cations are the most reactive species. The reaction of neutral and positive hydride radicals with carbon nitride substrates might be preferably accomplished through the formation of N–N bonds. Nevertheless, the negative hydride radicals may favor C–N bond formation with the substrate. Species containing C–N bonds were found to be preferable as precursors for chemical vapor deposition due to their high reactivity. The reactivity between gas-phase species and the carbon nitride clusters shows an increasing trend with the cluster size, indicating the ease of carbon nitride formation after its nucleation. Our results also show that CN radical possesses higher reactivity than C and N atoms and thus might be a good precursor for physical vapor deposition of carbon nitride films.

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I. INTRODUCTION

Since crystalline carbon nitride was predicted to possess extreme hardness,[1] considerable efforts have been made to search for this material using various experimental[2–7] and theoretical[8–10] approaches. Some experimental approaches are directly analogous to the chemical vapor deposition (CVD) method used in the successful growth of diamond films.[11] There are a large number of attempts to synthesize several carbon nitride phases. Particular attention has been paid to the β-C_3N_4 phase because this phase has been theoretically predicted to be harder than the hardest known material, diamond. Up until now, there is no credible evidence for a successful synthesis of crystalline β-C_3N_4 material.[12–14] Obviously, to develop a successful synthesis method, a deeper understanding of the formation mechanism of solid carbon nitride is needed. Thus far, most theoretical studies have focused mainly on the elucidation of the relative stability, structures, and physical properties of different crystalline phases of carbon nitride.[15–17] There is little information about how to synthesize crystalline carbon nitride efficiently and how to overcome difficulties encountered in synthesis.

In the growth of carbon nitride by CVD, the reactive carbon and nitrogen species are usually created by means of thermal or plasma-assisted decomposition before diffusing onto a specific substrate surface. This approach is expected to allow atoms to self-assemble into a crystalline solid so as to avoid the amorphization due to heavy ion bombardment in some thin film growth approaches. However, to synthesize the crystalline β-C_3N_4 material by CVD techniques, some fundamental issues have to be addressed. They include the possibility of self-assembling of carbon and nitrogen hydride species on a carbon nitride substrate, the identification of species which can easily self-assemble on a carbon nitride substrate, and the way to increase the reaction probability of species on the substrate. To address these issues, the study of the interactions between species and between species and the substrate within the framework of molecular orbital interaction is necessary and very useful.

In this work, we perform first-principle calculations to obtain the relative differences in the frontier orbital energies of various carbon hydride and nitrogen hydride species as well as the clusters of pseudocubic and β phases of carbon nitride (pc-C_3N_4,β-C_3N_4). The results are used to explore the associative reactions between radicals as well as reactions between radicals and substrates so as to throw light on their relative reactivity and to supply useful information which may guide the experimental synthesis of carbon nitride thin films.

II. THEORETICAL APPROACHES AND COMPUTATIONAL DETAILS

Two middle-size cluster models of $C_{12}N_{16}H_{24}$ for the pc phase and β phase, denoted as pc-C_3N_4(I) and β-C_3N_4(I) in Figs. 1(a) and 1(b), respectively (H atoms are not shown in Fig. 1), and two larger cluster models of these two phases, $C_{34}N_{36}H_{52}$ and $C_{36}N_{36}H_{60}$, denoted as pc-C_3N_4(II) and β-C_3N_4(II) in Figs. 1(c) and 1(d), were considered as the substrates in the present study. The latter two larger models were used to examine the size effects[18] on the results. The β-C_3N_4 structure considered here is the same as to the β-Si_3N_4 structure. Thus, the carbon atom in the model has four tetrahedral bonds (sp^3) with neighboring nitrogen atoms while the nitrogen atom forms three sp^2 bonds with neighboring carbon atoms. The pc-C_3N_4 model has the structure of the pseudocubic α-$CdIn_2Se_4$.[19]

The use of cluster models of the C_3N_4 phases is expected to provide insight into carbon nitride nucleation, since thin

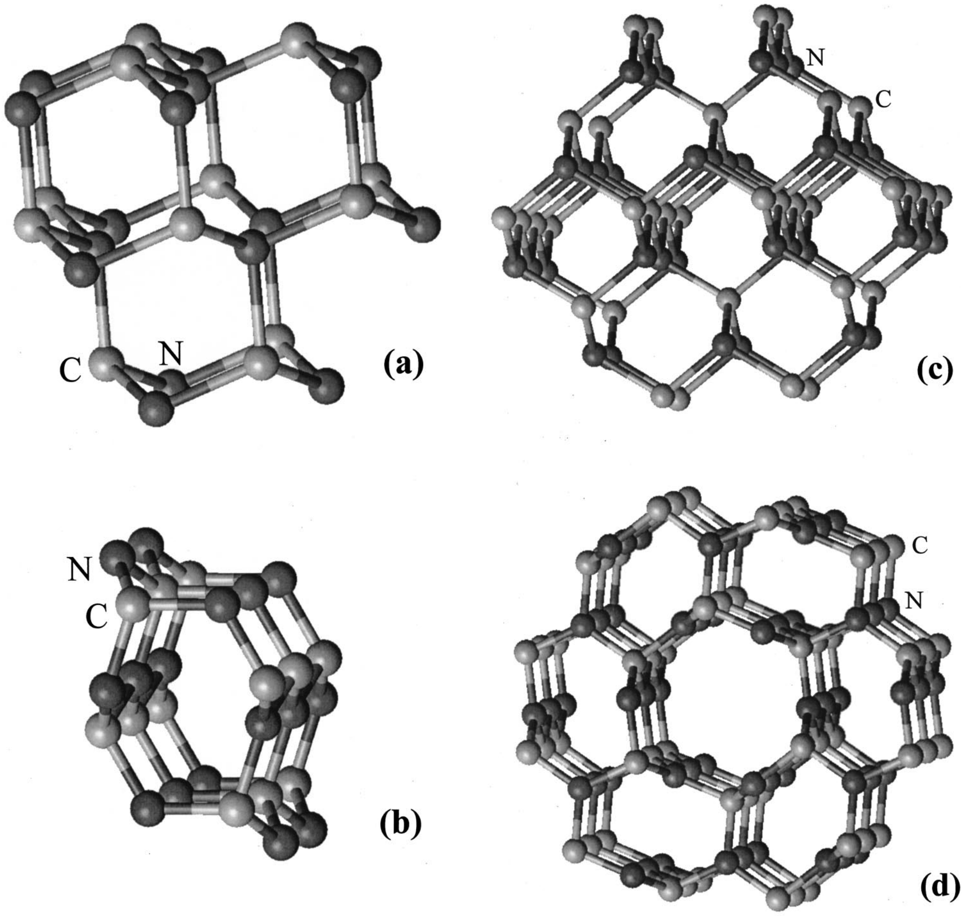


FIG. 1. Cluster models of two different phases of carbon nitride: (a) pc-C_3N_4(I), (b) β-C_3N_4(I), (c) pc-C_3N_4(II), and (d) β-C_3N_4(II).

film deposition usually starts from the nucleation of atoms into islands on the substrate surface, which was observed in the depositions of diamond films and other related films. After nucleation, the islands grow in size to form a continuous film. The hydrogen saturation of the cluster surface in our models is a realistic treatment, since the growth surface in CVD is saturated with species from the chemical vapor above, which usually contains hydrogen. In our calculation, all the structural models in Fig. 1 were fully geometrically optimized at HF/6-31G** level of calculation. Although, the geometries of the individual clusters could be far from bulklike, and even far from the geometries of thin film surfaces, the fully optimized structure can reflect the actually bonding arrangement of the nuclei in the initial depositions.

For all carbon hydride and nitrogen hydride species, calculations at both HF/6-31G** and HF/6-31++G** levels were performed to explore the effects of basis sets on their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Calculations at QCISD(T)/6-31G** and QCISD(T)/6-31++G** levels were also done for some species to compare the effects of configuration interaction on the HOMO and LUMO. All calculations were carried out using the GAUSSIAN 94 package.[20]

The effect of including the diffuse functions in the basis sets on HOMO and LUMO energies is shown in Table I for different species calculated at HF/6-31++G** level. For all neutrals and cations of both carbon hydride and nitrogen hydride species, diffuse functions have only a slight effect (a difference of less than 0.25 eV) on their HOMO energies. In contrast, the effect of diffuse functions is important for NH_1^-, NH_2^-, and NH_3^-, as the HOMO energies are decreased by about 0.004, 1.284, and 3.892 eV, respectively. The inclusion of diffuse functions also caused decreases of HOMO energies by about 1.804, 0.832, and 0.045 eV for CH_1^-, CH_2^-, and CH_3^-, respectively. However, the diffuse functions have strong effects on the LUMO energies of all the species considered except for the cations. The effect is especially significant for anions. Similar effects have been observed in some previous work.[21,22] Though different species show different decreases in LUMO energies, the overall trend found in this work is that, the more H atoms the species have, the larger is the decrease in the LUMO energy for all neutral and anions. The largest decrease in the energy of the LUMO was found in the anions, in which the decrease is 9.5 eV for NH_3^-. In determination of the relative reactivity of different species, anions are regarded as electron donors, the reactivity of which is generally related to the energies of their HOMO's.[23,24] Higher HOMO energies would lead to higher covalent reactivity which is related to the donor's capability of donating electrons, according to the general theory of reactivity.[25–27] Therefore, the large LUMO energy variation of anions (the electron donor) due to the inclusion of diffuse function may not affect the sequence of relative reactivity based on the HOMO energies obtained in HF/6-31++G** calculations.

TABLE I. HOMO and LUMO energies of different species calculated at HF/6-31++G** level. The diff(H)-(H) and diff(L)-(L) represent the differences in orbital energies obtained using HF/6-31++G** and HF/6-31G** theories for HOMO and LUMO, respectively.

Species	HOMO (a.u.)	LUMO (a.u.)	Diff(H)-(H) (eV)	Diff(L)-(L) (eV)
CH_4	−0.5464	0.0436	−0.042	−5.807
CH_3	−0.2372	−0.0030	−0.146	−4.337
CH_2	−0.5870	0.0276	−0.157	−1.236
CH_1	−0.4220	0.0203	−0.169	−1.097
NH_3	−0.4217	0.0435	−0.086	−4.918
NH_2	−0.4578	0.0437	−0.100	−2.748
NH_1	−0.4431	0.0121	−0.244	−1.011
$CH_3{}^-$	0.0011	0.1894	−0.045	−8.885
$CH_2{}^-$	−0.0404	0.1904	−0.832	−7.925
$CH_1{}^-$	−0.0133	0.1935	−1.804	−6.234
$NH_3{}^-$	0.0413	0.1808	−3.892	−9.543
$NH_2{}^-$	−0.0457	0.2047	−1.284	−8.722
$NH_1{}^-$	−0.0087	0.2070	−0.004	−9.496
$CH_3{}^+$	−0.9544	−0.2857	0.024	−0.156
$CH_2{}^+$	−0.8474	−0.2795	0.023	−0.175
$CH_1{}^+$	−0.8756	−0.3317	−0.001	−0.092
$NH_3{}^+$	−1.0394	−2.2513	0.015	−0.428
$NH_2{}^+$	−0.9243	−0.3650	0.015	−0.103
$NH_1{}^+$	−1.0030	−0.3804	0.037	−0.046

For electron acceptors, the reactivity of which is determined based on the LUMO energies, the dramatic LUMO energy decrease indicates that the results are unreasonable. Guerra[21] calculated the negative electron affinity (EA) of various small molecules with 6-31G* and 6-31+G* at Hartree-Fock self-consistent field and fourth-order Møller-Plesset levels and found that the use of diffuse functions in the 6-31+G* basis set led to meaningless values of negative EAs. Table II shows the calculated orbital eigenvalues, $-\varepsilon_{\mathrm{LUMO}}$ of some selected neutral compounds and $-\varepsilon_{\mathrm{HOMO}}$ of their respective anions with the same geometrical structures, and the experimental values of electron affinities (EA's).[28–31] According to Koopmans' theorem,[32] EA is approximately equal to $-\varepsilon_{\mathrm{LUMO}}$ of the neutral compounds or $-\varepsilon_{\mathrm{HOMO}}$ of the respective anions. It can be seen that both the $-\varepsilon_{\mathrm{LUMO}}$ of the neutral compounds [denoted as $-\varepsilon(\mathrm{A})_{\mathrm{LUMO}}$ for molecule ''A''] and $-\varepsilon_{\mathrm{HOMO}}$ of the corresponding anions [denoted as $-\varepsilon(\mathrm{A}^-)_{\mathrm{HOMO}}$] calculated at HF/6-31G** level qualitatively agree with the experimental EA values. The differences between the theoretical values of $-\varepsilon(\mathrm{A})_{\mathrm{LUMO}}$, $-\varepsilon(\mathrm{A}^-)_{\mathrm{HOMO}}$ and the experimental EA's can be attributed to the neglect of geometrical relaxation and electron correlation energy which could influence the EA to an extent dependent on the electronic structures. However, when two diffuse functions are added to the 6-31G**, both the $-\varepsilon(\mathrm{A})_{\mathrm{LUMO}}$ and $-\varepsilon(\mathrm{A}^-)_{\mathrm{HOMO}}$ calculated (now at HF/6-31++G** level) show large deviations from the respective experimental (EA's). This indicates that the orbital eigenvalues obtained at HF/6-31G** level of theory are more reasonable than those obtained at HF/6-31++G**. Guerra[21] ascribed this discrepancy to that the extra electron is mainly localized at the diffuse atomic orbitals and does not experience the repulsive short-range potential. As a result, the frontier orbital energies obtained using 6-31++G** basis set are not accurate enough for comparing the relative reactivity of electron acceptors based on frontier orbital theory.

In order to consider the electron correlation effect on the HOMO and LUMO energies, calculations at QCISD(T)/6-31G** and QCISD(T)/6-31++G** levels of theory were performed for some species which are relatively sensitive to the selection of basis sets at HF level of theory. In QCISD(T) calculations, quadratic configuration interaction including single and double substitutions with triple contributions to energy[33] were considered. The results compared with those at the HF level are shown in Table III. In both HF and QCISD(T) calculations, the diffuse functions have considerable effect on the LUMO energies. However, the differences in energies of HOMO and LUMO calculated using HF from those using QCISD(T) are less than 0.2 eV for all the considered species when the same basis set is used in the calculations.

TABLE II. The calculated eigenvalues $-\varepsilon_{\mathrm{LUMO}}$ of the neutral compounds and $-\varepsilon_{\mathrm{HOMO}}$ of the respective anions at the same geometry in comparison to the experimental EA values. All data are given in electron volts.

Molecule (A)	$-\varepsilon(\mathrm{A}^-)_{\mathrm{HOMO}}$ at HF/6-31G**	$-\varepsilon(\mathrm{A})_{\mathrm{LUMO}}$ at HF/6-31G**	$\varepsilon(\mathrm{A}^-)_{\mathrm{HOMO}}$ at HF/6-31++G**	$\varepsilon(\mathrm{A})_{\mathrm{LUMO}}$ at HF/6-31++G**	EA(expt)
CH_4	−6.5	−7.0	−1.2	−1.2	−8.0[a]
CH_3NH_2	−5.6	−6.3	−1.1	−1.1	−8.97[b]
CH_3F	−6.0	−6.8	−1.1	−1.1	−6.2[c]
CH_3Cl	−3.4	−5.3	−1.0	−1.1	−3.45[d]

[a] Reference 28.

[b] Reference 29.

[c] Reference 30.

[d] Reference 31.

TABLE III. Comparison of HOMO and LUMO energies of some species calculated using HF and QCISD(T) methods. HQ and HH represent HOMO energies obtained using QCISD(T) and HF methods, respectively; LQ and LH represent the respective LUMO energies.

	HOMO (a.u.)	LUMO (a.u.)	HOMO (a.u.)	LUMO (a.u.)	HQ-HH (eV)	LQ-LH (eV)
Method	QCISD(T)/6-31G**		HF/6-31G**			
CH_4	−0.5434	0.2561	−0.5448	0.2570	0.038	−0.025
CH_3	−0.3834	0.1563	−0.3832	0.1564	−0.005	−0.003
NH_3	−0.4241	0.2202	−0.4185	0.2242	−0.152	−0.109
NH_3^-	−0.1457	0.4907	−0.1414	0.4938	−0.117	−0.084
Method	QCISD(T)/6-31++G**		HF/6-31++G**			
CH_4	−0.5450	0.0436	−0.5464	0.0436	0.038	0
CH_3	−0.3832	0.0480	−0.3830	0.0481	−0.005	−0.003
NH_3	−0.4250	0.0429	−0.4217	0.0435	−0.090	−0.016
NH_3^-	0.0406	0.1812	0.0413	0.1808	−0.019	0.011

Based on the above-mentioned analysis and comparison, the calculations of HOMO and LUMO energies in this work have therefore been carried out using HF theory with the 6-31G** basis set.

III. RESULTS AND DISCUSSION

A. Reactions of species/species coupling

The possible interactions among species in CVD that we considered in our study include (1) neutral/neutral; (2) anion/anion; and (3) cation/cation. The reactions between species with different signs of charge are not studied here since those species could be efficiently separated using bias voltages in experiment. The following examinations of neutral species can help us to understand the reaction processes in CVD. As is well known, free radicals are typically highly reactive, leading to fast radical/radical reactions or radical/molecule reactions. The most common radical/radical reaction mode is coupling or cross-coupling reaction, which is essentially controlled by diffusion.[34] According to the frontier orbital theory,[35] the feasibility of a chemical reaction is inversely proportional to the HOMO-LUMO energy difference between the electron donor and acceptor. In order to identify the donor and acceptor during the interaction of two radicals, the charge distributions of isolated radicals and their coupling products as listed in Table IV were determined according to Mulliken population analysis. It is shown that the charge distributions of C, N, and H atoms are changed when the carbon hydride and nitrogen hydride groups are coupled. Electrons are transferred from the carbon hydride group to the nitrogen hydride group or from the carbon hydride group with more H atoms to the carbon hydride group with less H atoms. For instance, in the coupling products of CH_3NH_2 and CH_3CH_2, the charges of the NH_2 and CH_2 groups are respectively −0.175 and −0.009 a.u. Therefore, the nitrogen hydride radicals are usually acceptors in reactions between carbon hydride radicals and nitrogen hydride radicals and their LUMOs interact with the HOMOs of carbon hydride radi-

TABLE IV. Charge distributions in neutral species at HF/6-31G** level of calculation.

Species	Charge distribution			
CH_3	[C]: −0.384	[H1]: 0.128	[H2]: 0.128	[H3]: 0.128
CH_2	[C]: −0.196	[H1]: 0.098	[H2]: 0.098	
CH	[C]: −0.082	[H1]: 0.082		
NH_2	[N]: −0.522	[H1]: 0.261	[H2]: 0.261	
NH_1	[N]: −0.278	[H1]: 0.278		
CH_3NH_2	[CH_3]: 0.175	[NH_2]: −0.175		
CH_3NH	[CH_3]: 0.182	[NH]: −0.182		
CH_3CH_2	[CH_3]: 0.009	[CH_2]: −0.009		
CH_3CH	[CH_3]: 0.015	[CH]: −0.015		
CH_2NH_2	[CH_2]: 0.119	[NH_2]: −0.119		
CH_2NH	[CH_2]: 0.244	[NH]: −0.244		
$CHNH_2$	[CH]: 0.019	[NH_2]: −0.019		
CHNH	[CH]: 0.220	[NH]: −0.220		

TABLE V. The HOMO-LUMO energy differences between various neutral species at HF/6-31G** level of calculation. The rate constants cited are for a temperature of 298 K.

Electron donor	HOMO of donor (a.u.)	Electron acceptor	LUMO of acceptor (a.u.)	Differences (eV)	Rate constant (cm^3/mol s)
CH_3	−0.3832	NH_2	0.1447	14.37	
		NH	0.0492	11.77	
		CH_3	0.1563	14.68	2.83×10^{13} [a]
		CH_2	0.1463	14.41	3.01×10^{13} [b]
		CH	0.0606	12.08	
CH_2	−0.4072	NH_2	0.1447	15.02	
		NH	0.0492	12.42	
		CH_2	0.1463	15.06	3.19×10^{13} [c]
		CH	0.0606	12.73	
CH	−0.4158	NH_2	0.1447	15.25	
		NH	0.0492	12.65	
		CH	0.0606	12.96	
NH_2	−0.4541	NH_2	0.1447	16.29	2×10^{09} [d]
		NH	0.0492	13.70	8×10^{13} [d]
NH	−0.4341	NH	0.0492	13.15	

[a] Reference 36.
[b] Reference 37.
[c] Reference 38.
[d] Reference 39.

cals. In reactions between two carbon hydride radicals, the radicals with more H atoms are the electron donors. Further examination shows that the $HOMO_A$-$LUMO_B$ energy difference of donor ''*A*'' and acceptor ''*B*'' identified in this approach is in general smaller than the $HOMO_B$-$LUMO_A$ energy difference. As a result, apart from looking at the charge distributions, we can alternatively identify the donors and acceptors in reactions by looking for a smaller HOMO-LUMO energy difference.

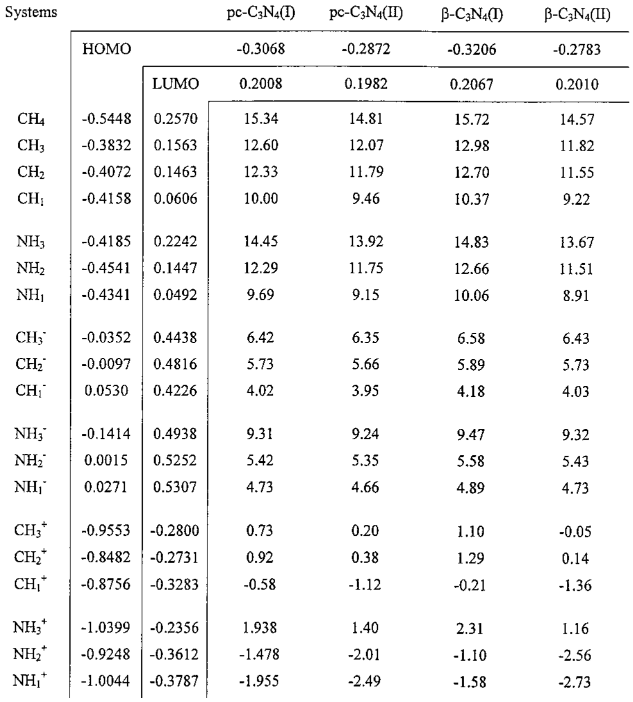
After identification of donors and acceptors in reactions according to the above-mentioned procedures, the HOMO-LUMO energy differences (shown in Table V) between different neutral radicals were compared to determine their relative reactivities. The HOMO-LUMO energy differences of reactions between CH_3 radical and CH_3, CH_2, NH_2, CH as well as NH radicals are, respectively, 14.68, 14.41, 14.37, 12.08 and 11.77 eV, while the HOMO-LUMO energy differences for coupling reactions of CH_2 with CH and NH are about 2.5 eV lower than those of CH_2 with NH_2 and CH_2. The coupling reaction of NH_2/NH_2 has a larger HOMO-LUMO energy difference (16.29 eV) because of the repulsion between lone pair electrons on the two N atoms. In order to demonstrate the reliability of the present approach and the reactivity determined accordingly, some rate constants of the reactions are cited from Refs. 36–39 in Table V. Clearly the rate constants are closely related to the HOMO-LUMO energy differences. A larger HOMO-LUMO energy difference leads to a smaller rate constant and implies a lower reactivity. For example, since the HOMO-LUMO energy difference between CH_3 and CH_3 is smaller than that between NH_2 and NH_2, the rate constant of the CH_3+CH_3 reaction is larger than that of the NH_2+NH_2 at room temperature. A similar trend is found in other systems except for the CH_2/CH_2 reaction.

B. Relative reactivity of different species with substrates

Table VI shows the HOMO-LUMO energy differences between different species and substrates obtained at HF/6-31G** level. For all four substrates simulated by the cluster models, the trends of relative reactivities of the species with the substrates are the same. When the cluster size increases, the reactivity of a species increases due to the decrease of the HOMO-LUMO energy difference between the substrate and the species. Since the initial deposition of carbon nitride may be in an island-like nucleation mode, the cluster-size effect indicates that the difficulty of carbon nitride formation would be reduced when the cluster size is increased. This is in good agreement with experimental findings during the depositions of diamond and other related materials that the most difficult step is nucleation in the initial stage of deposition. It is expected that after a continuous film is formed the deposition rate may reach the maximum, as the reactivity is the highest when the cluster size is the largest.

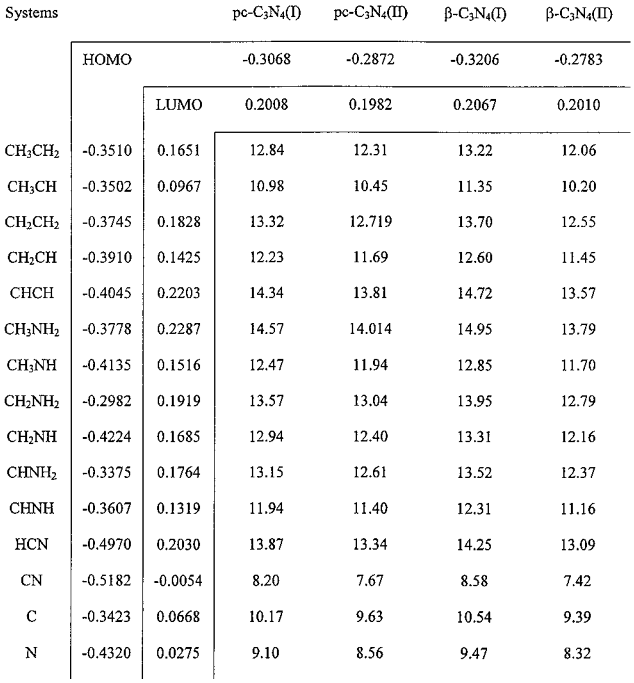
As listed in Table VI, the HOMO-LUMO energy differences between CH_4 and the substrates are about 3.0 eV larger than those between CH_3, CH_2, CH_1, and substrates, showing that CH_4 is more inert than other radicals. Slightly higher reactivities among the nitrogen hydrides than those among

TABLE VI. The HOMO-LUMO energy difference (in eV) between the selected species and the substrate at HF/6-31G** level of calculation. Note that the negative ions were considered as electron donors, while all the other species were considered as electron acceptors. The HOMO and LUMO energies (in a.u.) of the various species as well as pseudocubic (pc-C_3N_4) and β-phase carbon nitride (β-C_3N_4) (models I and II) are also listed, respectively.



Systems			pc-C_3N_4(I)	pc-C_3N_4(II)	β-C_3N_4(I)	β-C_3N_4(II)
	HOMO		-0.3068	-0.2872	-0.3206	-0.2783
		LUMO	0.2008	0.1982	0.2067	0.2010
CH_4	-0.5448	0.2570	15.34	14.81	15.72	14.57
CH_3	-0.3832	0.1563	12.60	12.07	12.98	11.82
CH_2	-0.4072	0.1463	12.33	11.79	12.70	11.55
CH_1	-0.4158	0.0606	10.00	9.46	10.37	9.22
NH_3	-0.4185	0.2242	14.45	13.92	14.83	13.67
NH_2	-0.4541	0.1447	12.29	11.75	12.66	11.51
NH_1	-0.4341	0.0492	9.69	9.15	10.06	8.91
CH_3^-	-0.0352	0.4438	6.42	6.35	6.58	6.43
CH_2^-	-0.0097	0.4816	5.73	5.66	5.89	5.73
CH_1^-	0.0530	0.4226	4.02	3.95	4.18	4.03
NH_3^-	-0.1414	0.4938	9.31	9.24	9.47	9.32
NH_2^-	0.0015	0.5252	5.42	5.35	5.58	5.43
NH_1^-	0.0271	0.5307	4.73	4.66	4.89	4.73
CH_3^+	-0.9553	-0.2800	0.73	0.20	1.10	-0.05
CH_2^+	-0.8482	-0.2731	0.92	0.38	1.29	0.14
CH_1^+	-0.8756	-0.3283	-0.58	-1.12	-0.21	-1.36
NH_3^+	-1.0399	-0.2356	1.938	1.40	2.31	1.16
NH_2^+	-0.9248	-0.3612	-1.478	-2.01	-1.10	-2.56
NH_1^+	-1.0044	-0.3787	-1.955	-2.49	-1.58	-2.73

TABLE VII. The HOMO (donor)-LUMO (acceptor) energy difference (in eV) between the C–N bond containing species (as well as C and N atoms) and the substrate at HF/6-31G** level of calculation. Note that all species were considered as electron acceptors. The HOMO and LUMO energies (in a.u.) of the various species as well as pseudocubic (pc-C_8N_4) and β-phase carbon nitride (β-C_3N_4) (models I and II) are also listed, respectively.



Systems			pc-C_3N_4(I)	pc-C_3N_4(II)	β-C_3N_4(I)	β-C_3N_4(II)
	HOMO		-0.3068	-0.2872	-0.3206	-0.2783
		LUMO	0.2008	0.1982	0.2067	0.2010
CH_3CH_2	-0.3510	0.1651	12.84	12.31	13.22	12.06
CH_3CH	-0.3502	0.0967	10.98	10.45	11.35	10.20
CH_2CH_2	-0.3745	0.1828	13.32	12.719	13.70	12.55
CH_2CH	-0.3910	0.1425	12.23	11.69	12.60	11.45
CHCH	-0.4045	0.2203	14.34	13.81	14.72	13.57
CH_3NH_2	-0.3778	0.2287	14.57	14.014	14.95	13.79
CH_3NH	-0.4135	0.1516	12.47	11.94	12.85	11.70
CH_2NH_2	-0.2982	0.1919	13.57	13.04	13.95	12.79
CH_2NH	-0.4224	0.1685	12.94	12.40	13.31	12.16
$CHNH_2$	-0.3375	0.1764	13.15	12.61	13.52	12.37
CHNH	-0.3607	0.1319	11.94	11.40	12.31	11.16
HCN	-0.4970	0.2030	13.87	13.34	14.25	13.09
CN	-0.5182	-0.0054	8.20	7.67	8.58	7.42
C	-0.3423	0.0668	10.17	9.63	10.54	9.39
N	-0.4320	0.0275	9.10	8.56	9.47	8.32

carbon hydrides are observed, indicating more chances for neutral nitrogen hydride species to react with substrates than for the neutral carbon hydrides before being reacting with other radicals. For the cations, CH_1^+, CH_2^+, and CH_3^+, the HOMO-LUMO energy differences between these species and pc-C_3N_4 and β-C_3N_4 substrates are below 1 and 1.3 eV, respectively, showing much higher reactivities than their neutral species with the substrates. Higher reactivities in cations than the corresponding neutral radicals are related to the structure weakening and energy increase due to additional electrons.[34] In general, cations appear to be more reactive than the corresponding anion radicals. Therefore, during the growth of carbon nitride films, the greater the number of cations in the reactants, the faster the reaction rate. For the anions listed in Table VI, the energy difference increases by about 1 eV when the number of H atoms is increased from CH_1^- to CH_3^- for both kinds of substrates. However, the energy difference between the HOMO of NH_3^- and the LUMO of substrates is about 3 eV larger than that of CH_3^- and about 4 eV larger than that of NH_2^-. Their relative reactivities lie in between the cation and the neutral species. The sequence of relative reactivity according to the HOMO-LUMO energy differences ranged from high to low for the anions is: $NH_1^- \cong CH_1^- > NH_2^- \cong CH_2^- > CH_3^- > NH_3^-$. The similar phenomenon that ionic species have higher chemical reactivity was also found in nitrogen and boron hydride adsorptions on Si(001) substrate in boron nitride growth.[40]

C. Competitions between species/species reactions and species/substrate reactions

In CVD processes, competition between radical/radical reactions and radical/substrate reactions is inevitable. In order to grow carbon nitride films on substrates, two conditions must be satisfied: (1) the radical/substrate reactions must be faster than radical–radical reactions and (2) the formation rate and probability of C–N bond on substrate must be faster and larger than those of C–C or N–N bonds. The following discussion of examples would help clarify the competitive reactions. Comparing the results in Tables V and VI, it is found that all of the HOMO-LUMO energy differences among radicals (CH_3, CH_2 and CH or CH_3, CH_2, CH, NH_2, and NH) are similar to or slightly higher than those between radicals (CH_3, CH_2, and CH) and the substrates. However, for NH_2 and NH radicals, the HOMO-LUMO energy differences in NH_2/NH_2 and NH/NH systems are about 3–4 eV more than the values in systems of NH_2/substrates and NH/substrates. The results show that the sticking of nitrogen hydrides on substrates may dominate in the CVD processes. In analyzing the molecular orbital coefficients of pc-C_3N_4

and β-C_3N_4 models, the main components of their HOMO's were found to localize at $2p$ atomic orbitals of surface nitrogen atoms, especially at $2p_z$ orbitals. On the other hand, the LUMO's of neutral nitrogen hydride species and the cations mainly consist of p atomic orbitals of N. This indicates that the dominant interactions between nitrogen hydride radicals (both the neutral and cation) and the pc-C_3N_4 or β-C_3N_4 substrates are through interactions between their N atomic orbitals. This does not favor the C–N bond formation on the substrates. Thus, we conclude that the growth of carbon nitride film is difficult using only small carbon and nitrogen hydride radicals or their cations. However, the main components of LUMO's of pc-C_3N_4 and β-C_3N_4 are *sp* hybrid orbitals of N and C atoms as well as *s* orbitals of H atoms, while the HOMO's of the hydride anions are composed of *sp* hybrid orbitals of N or C and the *s* orbital of H atoms, indicating that carbon nitride films may be easier to form if anions are used in CVD processes.

D. The interaction of C–N bond containing radicals with carbon nitride substrates

As indicated in the preceding section, the interaction of neutral carbon and nitrogen hydrides with substrates does not favor the formation of C–N bonds. It is necessary to develop new approaches to the formation of carbon nitride films for deposition processes in which neutral radicals are mainly produced, e.g., hot-filament CVD. To find appropriate approaches, we have further investigated the interaction of C–N bond containing radicals with substrates. Methylamine (CH_3NH_2) and its radicals CH_3NH, CH_2NH_2, CH_2NH, CHNH, and CN as well as some C–C containing species were considered. The energy differences between the LUMO's of these species and the HOMO's of substrates are shown in Table VII. The HOMO-LUMO energy differences for CH_3NH_2, CH_2NH_2, and HCN are found to be the largest among the C–N containing compounds. These species should be carefully decomposed or avoided in the CVD process. Although, CH_3NH, CH_2NH, and CHNH have similarly high reactivity, CH_3NH is probably preferred for forming N–N or N–H bond on substrates because the C atom is saturated. In addition, the chemical reactivities of C–N bond containing species are generally slightly lower than those of C–C containing species. The radical containing C–C bond will compete with species containing C–N bond during the growth process of carbon nitrides, and thus the contamination of precursors by C–C containing species should be avoided in order to achieve a pure phase of carbon nitride.

It is also noted that the CN radical is the most reactive radical containing C–N bond among the studied species shown in Table VII. However, this radical cannot easily be obtained through the decomposition of HCN in CVD process, since HCN is a rather stable product. Further, the reactivity of the CN radical is higher than that of C and N atoms, suggesting that it would be worthwhile to use CN species in physical vapor deposition so as to obtain carbon nitride phases instead of using only C and N sources.

IV. CONCLUSIONS

According to our analysis based on the frontier orbital theory, cations of carbon hydride and nitrogen hydride species possess high reactivities on the carbon nitride substrates of pseudocubic and β phases in associative deposition. The anions of these species have lower reactivity than their respective cations. The neutral species are more difficult to deposit on carbon nitride substrates than their ions. In CVD processes in which carbon hydride and nitrogen hydride radicals are involved, the neutral radicals and cations favor the formation of N–N bonds with the substrates while the anions favors the formation of C–N bonds with the substrate. Species containing C–N bonds have high reactivity and thus can be used as precursors for carbon nitride deposition. The reactivity between gas-phase species and the C_3N_4 grains will increase with the increase in the sizes of grains formed during the nucleation stage of deposition. In addition, the CN radical possesses higher reactivity than C and N atoms on the pc-C_3N_4 and β-C_3N_4 substrates and thus is suitable for being used as a precursor in PVD processes.

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