ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 6, pp. 1522–1527. © Pleiades Publishing, Ltd., 2015.

Theoretical Research on Structures of Aminopyrimidine Germanium(II) Precursors and Their Application in Film Formation[1]

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Received March 19, 2015

Abstract—Structures of aminopyrimidine Ge(II) precursors have been elucidated by density functional theory calculations. Calculation data indicated that the structure of aminopyrimidine Ge(II) compounds was four–coordinate with ten electrons. Thin film of Ge was deposited on Si wafer directly by means of home-made equipment and chemical vapor deposition technology. Aminopyrimidine Ge(II) precursors had excellent thermal properties and were suitable for potential membrane materials.

Keywords: aminopyrimidine germanium, precursors, DFT calculation, thin film

DOI: 10.1134/S1070363215060274

INTRODUCTION

Over the recent decades Ge(II) compounds are characterized by excellent thermal properties and volatility and have received considerable attention due to their application as precursors for phase–change random access memory (PRAM) [1–12]. Amidine Ge(II) derivatives are typical examples of compounds with high volatility and unique 10 electronic structure (Scheme 1, part **a**) [12–15]. Cowley and co-workers [16] reported the macrocyclic four-coordinate complexes of Ge(II). The authors [17] synthesized a series of new Ge(II) complexes by transamination of $Ge\{N(SiMe_3)_2\}$ with aminoaldimines or ethylidene-1,2-diamines with four-coordinate fashion and ten electrons (Scheme 1, parts **b** and **c**). Nevertheless, no studies clearly explained the relation between unique electronic structure and high volatility of such compounds. The current study objective was search for suitable precursors that would allow to determine the relation between structure of compounds and thin film properties.

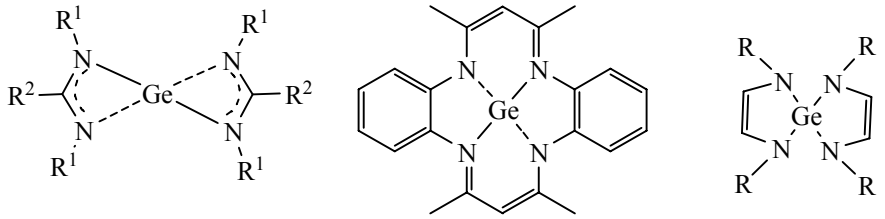
Aminopyrimidine ligand was selected as the one of high potential in coordination with Ge(II). The approach was supported by earlier publications [18] on a four-member ring structure of aminopyrimidinato Cd(II) compounds (Scheme 2, parts **a**, **b**) and [19] devoted to four-member ring structure of aminopyrimidinato titanium compound and its catalytic activity. Previously we had synthesized some aminopyrimidine Ge(II) complexes [20] that could be excellent precursors for making Ge thin films. However, the structures of those compounds could not be elucidated because of high volatility of aminopyrimidine Ge(II) complexes. Therefore, it was necessary to apply different methods, such as DFT calculation, to detect the relationship among the structure of products and their electronic structures and thermal properties. Herein, the structures of synthesized aminopyrimidine Ge(II) precursors have been elucidated with density functional theory calculation B3LYP and a basis set of 6-31G. Ge thin film was deposited on the Si wafer directly using the screened precursor and CVD technology.

RESULTS AND DISCUSSION

The optimized structure parameters, such as bond lengths, bond angles and dihedral angles of the synthesized compounds, were taken from SI file. The

[1] The text was submitted by the authors in English.

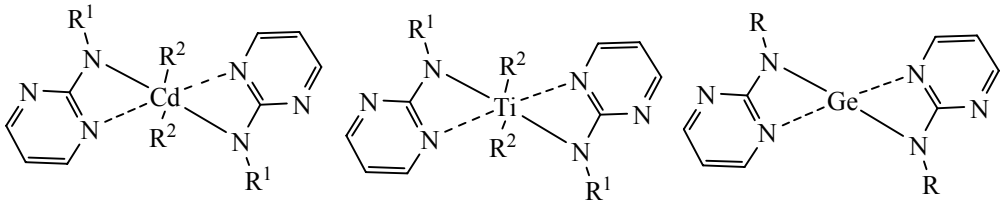
Scheme 1. Four-coordinate Ge(II) complexes with ten election structure.



a **b** **c**

[13–15] (**a**); [16] (**b**), [17] (**c**).

Scheme 2. Aminopyrimidine ligands complexes with four-member ring structure.



a **b** **c**

[18] (**a**); [19] (**b**), [This work] (**c**).

Ge–N bond distance (1.953–2.257 Å) was in the range of the reported data (1.982–2.300 Å) [12–15], albeit with a slight difference caused by changes of ligands and the coordination mode [21–28]. As expected, the reported data of bond distance and the calculation data supported the four-member ring structures. For example, the complex **IIc** was characterized by the Ge–N^{20} and Ge–N^{21} bonds length equal to 1.99 Å, which was a little shorter than the Ge–N^{2} and Ge–N^{11} bonds length (2.25 Å). The difference between bond lengths was due to distinction between the kinds of bonds. The bond angle N^{21}–Ge^{1}–N^{11} (62.550º) was very close to the data that had been reported earlier (62.29º–61.00º) [18–20]. The calculations supported the structure of aminopyrimidine Ge(II) compounds with four-coordinate fashion and ten electrons.

The charge distributions of Ge in the complexes **IIb** and **IIc** were 1.142 and 1.143 Å respectively, while in complex **IIa** it was 1.162 Å. Such apparent increase was attributed to conformation features. As a rule, the closer the ligands and Ge atoms get, the greater the partial electron density would be and Ge atoms would carry higher charge in order to maintain the complex neutral. For example, the ligands of complex **IIa** are closest to Ge atom among these three complexes and Ge atom possesses the highest charge.

More importantly, the charge distribution could confirm the complex structure. In the complex **IIa**, for example, the charges of N^{2} and N^{11} were –0.612 and –0.609 respectively, while those of N^{5} and N^{14} were –0.516 and –0.514 respectively. The big difference in charges between N^{2} and N^{5} demonstrated that only one N atom in pyrimidine ring was coordinated with central Ge, which suggested that the coordination caused electron density of N atoms to change. The above was true for N^{2} and N^{11} but not N^{5} and N^{14} (see table). All calculated data suggested that the bond lengths and angles in the products molecules were similar to the literature data and four N atoms participated in coordination confirming the proposed structures of the complexes [20].

Thermal properties of the complexes were studied and presented in Fig 3. Complex **IIa** was distinctive in many respects, including the second weight loss step in the TGA curve. Low thermal stability could be related to specific conformation and the electronic environment. The shorter Ge–N bond length could hinder the molecule ability to adjust to heating, whereby the bond was broken. In products **IIb** and **IIc** the substituent group was small enough to avoid the distortion and the Ge–N bond distance was long enough to fit the molecule change in the heating

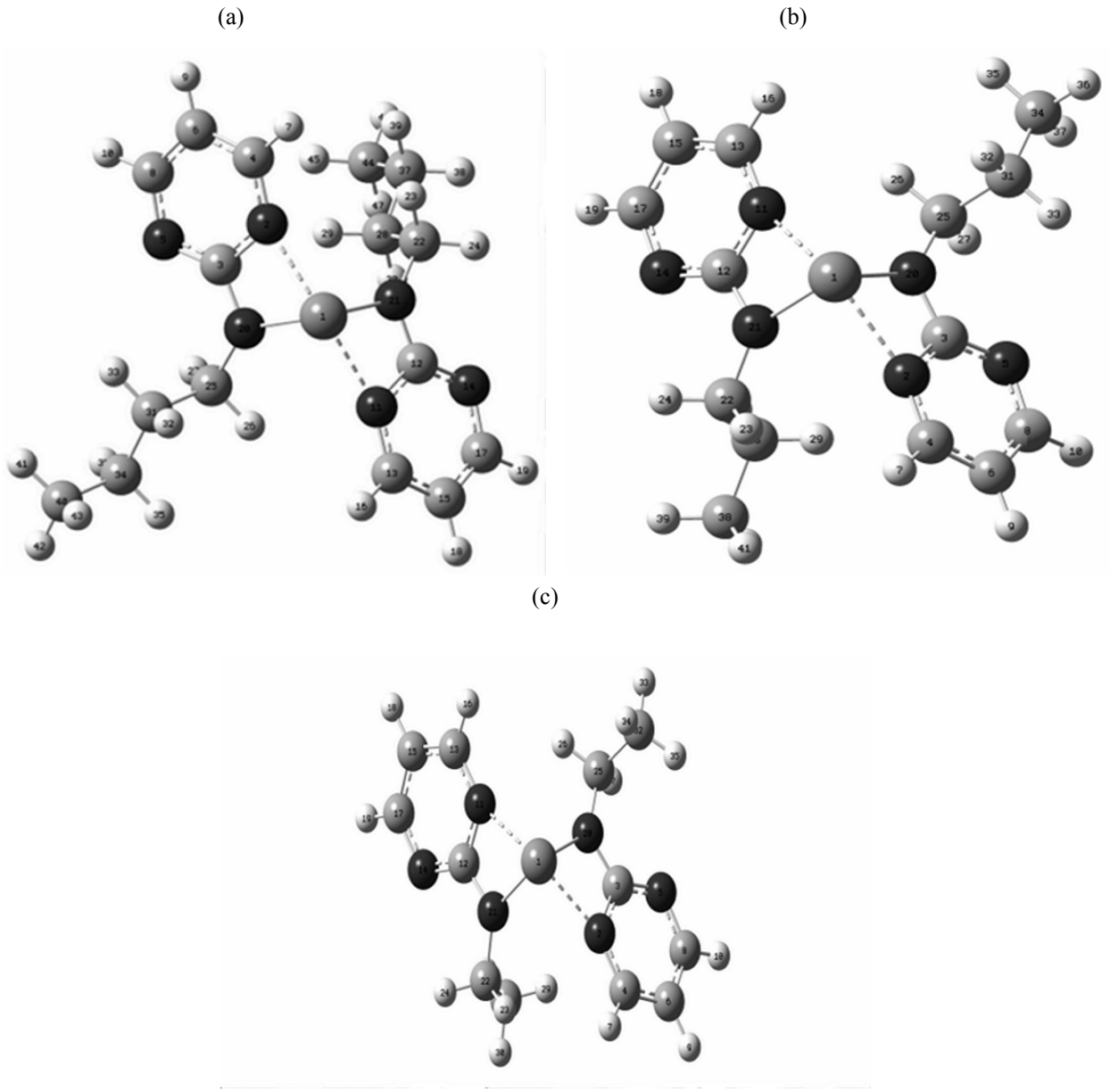


Fig. 1. The geometric structure optimization of compounds (a) **IIa,** (b) **IIb,** and (c) **IIc.**

process, so they possessed the stable thermal character and demonstrated similar TGA curves.

Thin film formation of the precursor **IIc** was studied. 5% H_2 in H_2/N_2 blended gas (reducing gas) was flown through the heating compartment at the rate 60 mL min^{-1}. Heating from room temperature to 500ºC was performed at the rate 30 deg min^{-1}. A metallic sheen on a silicon wafer was formed and characterized by SEM.

According to low magnification the film surface was not uniform. Upon amplification a flat area with no defects was observed. The experiments demonstrated that aminopyrimidine Ge(II) complexes were suitable precursors for potential membrane materials.

EXPERIMENTAL

Aminopyrimidine Ge(II) compounds were synthesized in accordance with the method presented

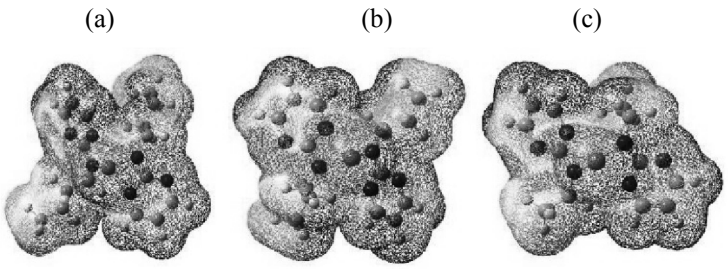


Fig. 2. Electron density of compounds (a) **IIa,** (b) **IIb,** and (c) **IIc.**

in the publication [20] by addition of a solution of lithium salt of respective ligands to a stirred solution of $GeCl_2$·dioxane in diethyl ether at low temperature (Scheme 3). Yellow powder of the corresponding product was obtained upon storage of the extract at –29°C overnight.

All calculations were carried out with GAMESS-US program [29, 30].

Thermogravimetric analysis was performed on a TGA apparatus. The complexes were placed in open alumina crucibles and heated from 30 to 800ºC with

Structural data for ground state of compounds **IIa–IIc** optimized with density functional theory B3LYP and a basis set of 6-31G

Parameters	**IIa**	Parameters	**IIb**	Parameters	**IIc**
Selected bond distances, Å					
$Ge^1–N^{20}$	1.95984	$Ge^1–N^{20}$	1.98958	$Ge^1–N^{20}$	1.99214
$Ge^1–N^{21}$	1.95364	$Ge^1–N^{21}$	1.99444	$Ge^1–N^{21}$	1.99339
$Ge^1–N^2$	2.19869	$Ge^1–N^2$	2.25707	$Ge^1–N^2$	2.25644
$Ge^1–N^{11}$	2.21667	$Ge^1–N^{11}$	2.25126	$Ge^1–N^{11}$	2.25412
Selected bond angles, deg					
$N^2–Ge^1–N^{20}$	64.543	$N^{21}–Ge^1–N^{11}$	62.602	$N^{21}–Ge^1–N^{11}$	62.550
$N^{21}–Ge^1–N^{11}$	64.390	$N^{20}–Ge^1–N^2$	62.569	$N^2–Ge^1–N^{20}$	62.550
$Ge^1–N^{20}–C^3$	100.993	$Ge^1–N^{21}–C^{12}$	100.570	$Ge^1–N^{21}–C^{12}$	100.703
$Ge^1–N^{21}–C^{12}$	101.465	$Ge^1–N^{20}–C^3$	100.761	$Ge^1–N^{20}–C^3$	100.715
$N^{20}–C^3–N^2$	106.190	$N^{21}–C^{12}–N^{11}$	109.159	$N^{11}–C^{12}–N^{21}$	109.147
$N^{21}–C^{12}–N^{11}$	106.411	$N^{20}–C^3–N^2$	109.128	$N^2–C^3–N^{20}$	109.156
$C^3–N^2–Ge^1$	88.199	$Ge^1–N^{11}–C^{12}$	87.640	$Ge^1–N^{11}–C^{12}$	87.582
$Ge^1–N^{11}–C^{12}$	87.733	$Ge^1–N^2–C^3$	87.423	$Ge^1–N^2–C^3$	87.490
$C^{22}–N^{21}–C^{12}$	122.672	$C^{12}–N^{21}–C^{22}$	123.694	$C^3–N^{20}–C^{25}$	123.749
$C^3–N^{20}–C^{25}$	122.972	$C^{25}–N^{20}–C^3$	123.880	$C^{12}–N^{21}–C^{22}$	123.743
Selected torsion angles, deg					
$N^{11}–Ge^1–N^{20}–C^3$	–156.859	$N^2–Ge^1–N^{21}–C^{12}$	–146.200	$N^2–Ge^1–N^{21}–C^{12}$	–145.648
$N^2–Ge^1–N^{21}–C^{12}$	–155.209	$N^{11}–Ge^1–N^{20}–C^3$	–147.290	$N^{11}–Ge^1–N^{20}–C^3$	–146.441

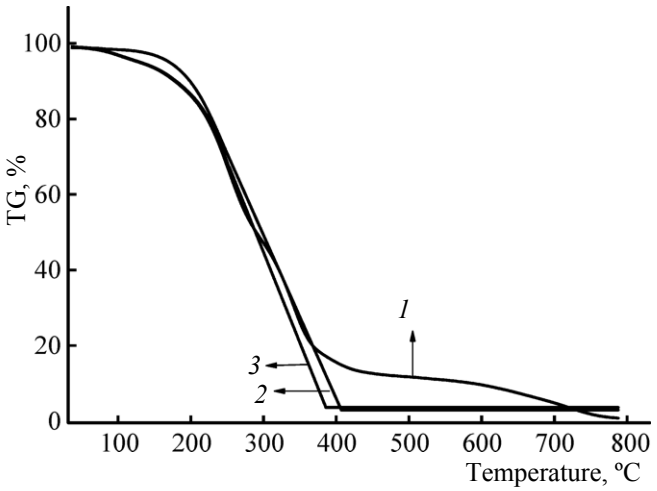


Fig. 3. TGA curves of compounds (*1*) **IIa,** (*2*) **IIb,** and (*3*) **IIc.**

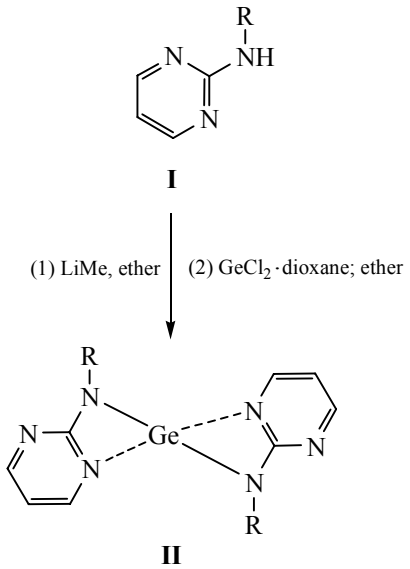
the heating rate of 10 deg min^{-1} under Ar flow rate 80 mL min^{-1}. Temperature was measured by means of a Pt–Pt/Rh thermocouple with accuracy of ±0.5ºC. Ge thin film was deposited on Si directly with the compound **IIc** with the help of the home-made equipment.

CONCLUSIONS

In summary, the structures of complexes were elucidated by DFT calculations that allowed to establish the relationship between structure and thermal property of products. The data supported the structure of aminopyrimidine Ge(II) compounds with four-coordinate fashion and ten electrons. Ge thin film was deposited on the Si wafer directly using the screened precursor and CVD technology, thus suggesting that aminopyrimidine Ge(II) complexes were suitable precursors for potential membrane materials.

Supplementary data related to this article is available free of charge via the Internet.

Scheme 3. Synthesis of aminopyrimidine germanium(II) procursors.



R = *n*-Bu, 50% (**IIa**), *n*-Pr, 62% (**IIb**), Et, 40% (**IIc**).

ACKNOWLEDGMENTS

We gratefully acknowledge financial support of this work by the National Natural Science Foundation of China (no. 21371080), 333 Talent Project of Jiangsu Province (BRA2012165) and MOE & SAFEA for the 111 Project (B13025).

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