

行政院國家科學委員會專題研究計畫 成果報告

半導體氮(磷)化物化學蒸鍍中的自由基及中間物之結構,動力學及能階(3/3)(中加國合計畫)

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中文摘要

本三年計劃目前共發表 5 篇論文，預計尚有 2-4 篇可發表，成果豐碩。完成了 GeNNGe, Ge(NO), Ge(NO)₂ 之產生及其紅外光譜診斷，CH₂Cl₂ 及 CH₂Br₂ 之真空紫外光游離研究以及 CH₂CO 的共振多光子游離研究。目前正撰寫 Si(NO)及 Si(NO)₂ 之產生及其紅外光譜研究之論文。

關鍵詞：間質隔離，真空紫外光游離，共振多光子游離

英文摘要

In this 3-year project, we published 5 papers so far and expect to have 2-4 more publications. We have produced GeNNGe, Ge(NO), and Ge(NO)₂ in matrices and assigned its IR absorption spectrum. We also investigated VUV ionization of CH₂Cl₂ and CH₂Br₂, and the REMPI study of CH₂CO. Currently, we are writing a paper concerning IR spectra of Si(NO) and Si(NO)₂.

Keywords: matrix-isolation, VUV ionization, REMPI

1. **"Dissociative photoionization of CH₂Cl₂ and enthalpy of formation of CHCl⁺:**

Experiments and calculations", S.-Y. Chiang, M. Bahou, K. Sankaran, Y.-P. Lee, H.-F. Lu, and M.-D. Su, **J. Chem. Phys.** **118**, **62** (2003).

The dissociative photoionization of CH₂Cl₂ in a region ~11–20 eV was investigated with photoionization mass spectrometry using a synchrotron radiation source. Major fragment ions CH₂Cl⁺, CHCl⁺, and CCl⁺ were observed with their respective appearance energies at 12.08, 12.46, and 15.96 eV. Relative branching ratios as a function of photon energy were determined. Dissociative photoionization channels for formation of these three fragment ions are proposed based on comparison of determined appearance energies and energies predicted with the Gaussian-2 calculations. The principal dissociative process is direct breakage of the C–Cl bond to form CH₂Cl⁺+Cl; at greater energies formation of CHCl⁺ takes place via the CHCl⁺+HCl channel. Formation of CCl near the threshold at 15.96 eV may proceed via the CCl⁺+HCl+H channel rather than CCl⁺+H₂+Cl channel, but at greater energies the latter dominates. Enthalpy of formation at 0 K of CHCl⁺ is revised to 288.0±0.7 kcal mol⁻¹ based on our experimental results; the adiabatic ionization energy of CHCl is accordingly revised to 9.12±0.12 eV.

2. **"Isomers of Ge₂N₂: production and IR absorption of GeNNGe in solid N₂"**, M.

Bahou, K. Sankaran, Y.-J. Wu, Y.-P. Lee, D. Rayner, and B. Simard, **J. Chem. Phys.** **118**, **9710** (2003)

Crystalline germanium was ablated with light at 532 nm from a frequency-doubled Nd:YAG laser, and the resultant plume reacted with N₂ before deposition onto a substrate at 20 K. Multiple absorption lines at 891.8, 890.8, 890.4, 889.9, 889.4, 888.9, 888.4, 887.9, 887.5, and 887.0 cm⁻¹ that become enhanced after annealing of the matrix at 31 K are attributed to a species containing two Ge atoms in their isotopic variants: ⁷⁰Ge, ⁷²Ge, ⁷³Ge, ⁷⁴Ge, and ⁷⁶Ge. Replacing ¹⁴N₂ with a mixture of ¹⁴N₂ and ¹⁵N₂ yields an additional multiplet in the region 867.1–862.1 cm⁻¹, whereas reaction of the same mixture subjected to microwave discharge yields a further multiplet in the region 878.9–874.0 cm⁻¹. The isotopic pattern indicates that the vibrational mode is associated with a Ge–N stretching motion that involves two equivalent Ge atoms and two equivalent N atoms. Theoretical calculations with density-functional theories (B3LYP/6-311+G* and B3LYP/aug-cc-pVTZ) predict nine stable isomers of Ge₂N₂, with linear GeNNGe and asymmetric angular Ge(GeNN) having the least energies. Among calculated vibrational wave numbers, IR intensities, and isotopic shifts for all isomers of Ge₂N₂, only those predicted for the asymmetric Ge–N stretching mode of linear GeNNGe fit satisfactorily with experimental results. GeNNGe is likely formed from direct reaction of Ge₂ and N₂ rather than from two-step reactions involving GeNN or GeN.

3. **"Investigation of some Rydberg states of ketene by two-photon**

resonance-enhanced multiphoton-ionization spectroscopy", S. Wang, Y. Shi, S. Dénommée, B. Simard, and Y.-P. Lee, **J. Chem. Phys.** **119**, 7772 (2003).

Rydberg states of CH₂CO and CD₂CO in the 54 000–72 000 cm⁻¹ spectral range have been reinvestigated using two-photon resonance-enhanced multiphoton-ionization spectroscopy. Improved resolution and sensitivity has allowed for identifications of more Rydberg states than in previous work. Based on an analysis of rotational structures and quantum defects and a comparison with the results of theoretical calculations, transitions to the 3p_z, 4p_y, 4p_z, and 5p_y, three components of 4d, and two components of 4f Rydberg states with a ground-state ionic core (\tilde{X}^2B_1) are identified. Several transitions have been reassigned. Vibrational wave numbers indicate that the geometry of the [\tilde{X}^2B_1]3p_y (¹A₂) state is almost identical to that of the corresponding cation in its ground electronic state, with C_{2v} symmetry, whereas that of the [\tilde{X}^2B_1]3p_x (¹A₁) state differs significantly from those of the neutral molecule and the cation in their ground states, consistent with previous quantum chemical calculations that indicated that the [\tilde{X}^2B_1]3p_x (¹A₁) state has C_s symmetry. The energy ordering of the three components of the 3p Rydberg states is found to be 3p_x, 3p_y, 3p_z, in agreement with a previous theoretical prediction using the equation-of-motion coupled-cluster singles and doubles polarized basis set methods and a first-principles vibronic model simulation. Excitations of the vibrational modes of b₁ (e.g., =C=O out-of-plane bending, CH₂ or CD₂ wagging! and b₂ symmetries (e.g., C=C=O in-plane bending) are observed in several Rydberg states of CH₂CO and CD₂CO.

4. **"Experimental and *ab initio* studies of photoionization and dissociative photoionization of CH₂Br₂"**, S.-Y. Chiang, Y.-S. Fang, K. Sankaran, and Y.-P. Lee, **J. Chem. Phys.** **120**, 3270 (2004).

The dissociative photoionization of CH₂Br₂ in a region ~10–24 eV was investigated with photoionization mass spectroscopy using a synchrotron radiation source. An adiabatic ionization energy of 10.25 eV determined for CH₂Br₂ agrees satisfactorily with predictions of 10.26 and 10.25 eV with G₂ and G₃ methods, respectively. Observed major fragment ions CH₂Br⁺, CHBr⁺, and CBr⁺ show appearance energies at 11.22, 12.59, and 15.42 eV, respectively; minor fragment ions CHBr₂⁺, Br⁺, and CH₂⁺ appear at 12.64, 15.31, and 16.80

eV, respectively. Energies for formation of observed fragment ions and their neutral counterparts upon ionization of CH_2Br_2 are computed with G_2 and G_3 methods. Dissociative photoionization channels associated with six observed fragment ions are proposed based on comparison of determined appearance energies and predicted energies. An upper limit of $\Delta H_{f,298}^\circ(\text{CHBr}^+) \leq 300.7 \pm 1.5 \text{ kcal mol}^{-1}$ is derived experimentally; the adiabatic ionization energy of CHBr is thus derived to be $\leq 9.1760.23 \text{ eV}$. Literature values for $\Delta H_{f,298}^\circ(\text{CBr}^+) = 362.5 \text{ kcal mol}^{-1}$ and ionization energy of 10.43 eV for CBr are revised to be less than $332 \text{ kcal mol}^{-1}$ and 9.11 eV , respectively. Also based on a new experimental ionization energy, $\Delta H_{f,298}^\circ(\text{CH}_2\text{Br}_2^+)$ is revised to be $236.4 \pm 1.5 \text{ kcal mol}^{-1}$.

5. **"Isomers of GeNO and Ge(NO)₂ :Production and Infrared Absorption of GeNO and ONGeNO in Solid Ar"**, J.-B. Chou, M. Bahou, Y.-P. Lee, D. Rayner, and B. Simard, **J. Chem. Phys.** **123**, 054321 (2005).

Crystalline germanium was ablated with light at 532 nm from a frequency-doubled Nd:YAG laser, and the resultant plume reacted with NO before deposition onto a substrate at 13 K . Lines in group A at 1543.8 and 3059.7 cm^{-1} that become enhanced at the initial stage of irradiation at 308 or 193 nm and also after annealing are attributed to ν_1 and $2\nu_1$ of GeNO . Lines in group B at 1645.5 and 1482.8 cm^{-1} that become diminished after further irradiation of the matrix at 308 nm or 193 nm but become enhanced after annealing are attributed to symmetric NO -stretch (ν_1) and antisymmetric NO -stretch (ν_7) of ONGeNO . The assignments were derived based on wave numbers and isotopic ratios observed in experiments with ^{15}N - and ^{18}O -isotopic substitutions and predicted with quantum-chemical calculations. Quantum-chemical calculations with density-functional theories (B3LYP and BLYP/aug-cc-pVTZ) predict four stable isomers of GeNO , six isomers of Ge_2NO , and four isomers of $\text{Ge}(\text{NO})_2$, with linear GeNO , *cyc*- GeNGeO , and *cyc*- GeONNO having the least energies, respectively. Formation mechanisms of GeNO and ONGeNO are discussed. In addition, a weak line at 1417.0 cm^{-1} and two additional lines associated with minor matrix sites at 1423.0 and 1420.3 cm^{-1} are assigned to GeNO^- .