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Synthesis and Explosion Properties of Porous Silicon/Gadolinium Nitrate Energetic Composite

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In this paper, fresh porous silicon was prepared by electrochemical anodization method using a mixture of hydrofluoric acid and dinethylformamide as electrolyte. The obtained pores were loaded with $Gd(NO_3)_3·6H_2O$ oxidizer to create energetic material. Effect of the HF concentration on explosion properties was investigated by measurement of sound intensity and emission spectra of the explosion. The result shows that the optimal explosion property of the energetic material can be obtained when HF concentration is 31.4 wt % and the maximum colour temperature of the explosion reaches to 3495.1 K. Interaction between Si-H_x (x = 1, 2, 3) and $Gd(NO_3)_3$ in the energetic material was studied by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. A detailed demonstration for this interaction is presented.

Key Words: Composite, Explosion, Colour temperature, Binding energy.

INTRODUCTION

The fast combustion reaction of porous silicon immersed in nitric acid was discovered in 1992[1]. Since then, porous silicon/oxidizer systems have attracted comprehensive attention due to excellent performance in terms of energy release, ignition and mechanical properties. Explosive experiments based on porous silicon have been developed rapidly[2-4]. Various oxidizers, such as liquid oxygen, sulfur and strong oxidizing salts, were investigated[5-7]. Churaman *et al.*[8] demonstrated the mechanism of highly energetic behaviour of nano-crystalline porous silicon and the formation of O and OH radicals during the explosion. To achieve a higher efficiency of explosive reaction, effects of current densities, oxidation time, electrolyte composition, temperature and illumination on the porous silicon porosity have been studied. Becker *et al.*[9] proposed the energy output was dependent on the hydrogen termination of porous silicon. Recently, the interaction between S_2 molecule and Si - H_x (x = 1, 2, 3) in porous silicon was investigated using the B3LYP method of density functional theory with the LANL2DZ basis set[10].

Colour temperature of light induced by the explosion is considered as one of important parameters in the field of solid-explosive research[11]. The colour temperature of the explosion based on porous silicon/$Gd(NO_3)_3$ composite was estimated to be 2000 K by Mikulec *et al.*[3].

This paper reports on explosion properties of porous silicon/gadolinium nitrate energetic composite. The emission spectra of the explosion and corresponding chromaticity coordinates were investigated. FT-IR and XPS were used to analyze the interaction between porous silicon and oxidizer $Gd(NO_3)_3$. These studies provide useful information for higher explosive efficient energy composite.

EXPERIMENTAL

n-Type and 500 µm-thick silicon wafers with resistivity of 2-4 Ω cm were used. The individual chips were scribed 4 mm × 4 mm. Native oxide on the silicon surface was removed by 10 % HF. Porous silicon layers were prepared by the constant current electrochemical etching. A mixture of 40 % HF and 99.5 % DMF was used as an electrolyte. The volume ratios of two chemicals were 1:2, 1:1, 2:1, 3:1 and 4:1, so that the concentrations of HF were 14.4, 20.0, 28.4, 31.4 and 33.2 wt %. Volume of electrolyte was set at 40 mL. Constant current was supplied between two electrodes at 40 mA by direct current power supply (WYJ, 150V3A). Anodization was performed for 25 min and the whole etching process was lighted by a 300 W tungsten lamp. After etching, porous silicon was impregnated with 20 mL solution of $Gd(NO_3)_3$ in ethanol. Samples were allowed to dry in vacuum for 1 h, before performing any experiments.

Impulse precision sound level meter (HS5660C) and USB2000 Miniature Fiber Optic Spectrometer (Ocean Optics Inc.) with a fiber probe were used to characterize sound intensity and emission spectrum of the explosion. FT-IR (Nicollet 5DX) was utilized to analyze the chemical bonds in the freshly prepared porous silicon and composite. XPS (ESCALAB 250) was used to determine the elemental composition.

RESULTS AND DISCUSSION

Effect of HF concentration on the explosion properties: Explosion results of porous silicon/ $Gd(NO_3)_3$ composites prepared under different conditions are listed in Table-1. The concentrations of HF in electrolyte are 14.4, 20.0, 28.4, 31.4 and 33.2 wt %, respectively. Composites will suffer explosion when the concentration of HF is more than 28.4 wt %, but the violence degrees of reaction are different. Comparing to sound intensity index, we find that composite is better in terms of the explosion intensity when the concentration of HF in electrolyte is 31.4 wt % and the explosion phenomenon is shown in Fig. 1. The intense yellow light is emitted during the explosion. Some tiny particles are ejected vertically from the silicon surface and the porous silicon layer is completely damaged without silicon substrate body destroyed during the explosion. However, explosion phenomenon can't be observed when the concentration of HF is less than 28.4 wt %.

TABLE-1
EFFECT OF HF CONCENTRATION ON
EXPLOSIVE PROPERTIES OF COMPOSITE

HF conc. (wt %)	Description of explosion	Sound intensity (dB)	Damage to porous silicon layer
14.4	No explosion	–	No damage
22.0	No explosion	–	No damage
28.4	Weak explosion, faint spark	127	Local damage
31.4	Strong explosion, obvious spark	156	Holistic damage
33.2	Strong explosion, obvious spark	140	Holistic damage

Fig. 1. Explosion photograph of porous silicon impregnated with $Gd(NO_3)_3$

Spectra of the light emitted from the explosion of composites are recorded in Fig. 2. These emission spectra include several sharp peaks located in 400-680 nm with the same shapes, revealing similar interaction ways during the explosion. In addition, sample has the maximum emission intensity when the concentration of HF in electrolyte is 31.4 wt %, which is in agreement with results of sound intensity testing.

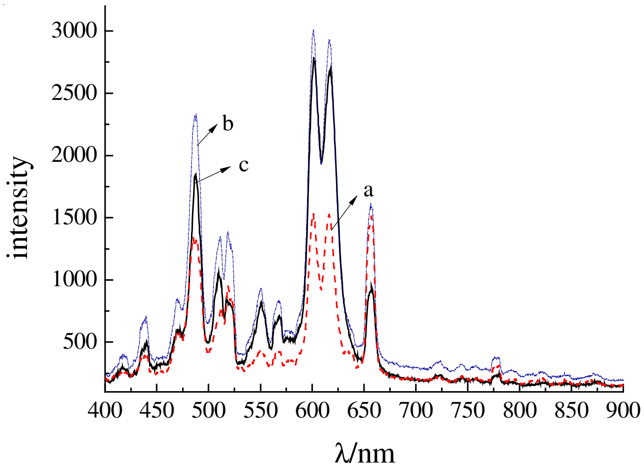

Fig. 2. Spectra of the light emitted from an explosion of composite, where composite was prepared when the concentrations of HF in electrolyte are (a) 28.4, (b) 31.4 and (c) 33.2 wt %, respectively

The chromaticity coordinate of three composites, calculated from the spectral data, is shown in corresponding chromaticity diagram depicted in Fig. 3. The correlated colour temperature of the explosion is evaluated from the chromaticity coordinate by McCamy's approximate formula[12]:

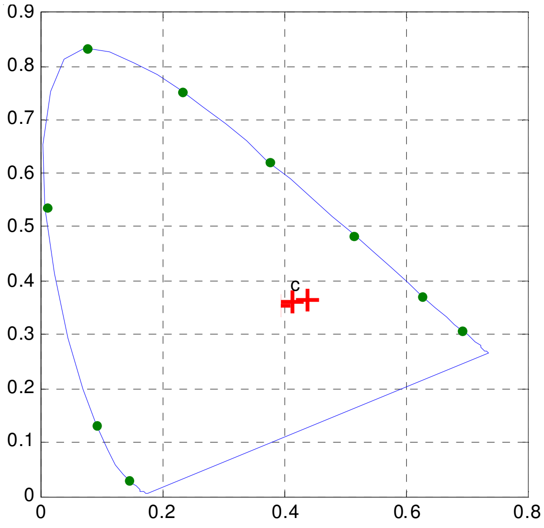

Fig. 3. Corresponding chromaticity diagram

$$\frac{T}{K} = -437n^3 + 3601n^2 - 6861n + 5514.3 \quad (1)$$

with

$$n = \frac{(x - 0.3320)}{(y - 0.1858)}$$

where x and y are chromaticity coordinate and the correlated colour temperatures are 2616.0, 3495.1 and 3060.4 K, respectively. It can be found that the explosion of sample prepared with HF concentration of 31.4 wt %, yields the maximum correlated colour temperature, which is much larger than the reported value[3].

FT-IR analysis: Fig. 4 shows the FT-IR spectra of the composite and fresh prepared porous silicon prepared with different HF concentrations, respectively. For samples (a) and (b), there are no obvious features of Si-H_x bonds. This is the

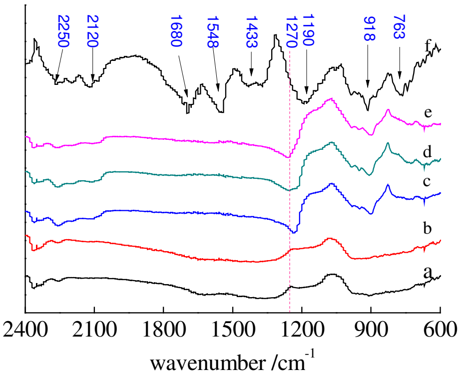

Fig. 4. FT-IR spectra of (a)-(e) fresh prepared porous silicon by different etchant compositions and (f) composite, where porous silicon was formed when the concentrations of HF in electrolyte are (a) 14.4, (b) 20.0, (c) 28.4, (d) 31.4 and (e) 33.2 wt %, respectively

reason why these samples don't suffer explosion when HF concentration in electrolyte is less than 22.0 wt %. For samples (c), (d) and (e), the peaks around 2250 cm^{-1} stem from OSi-H trembling and stretching mode and the broad peaks nearby 2120 cm^{-1} are attributed to Si-H$_x$ (x = 1, 2, 3) stretching modes[13-15]. The most interesting features are the ones from 1300-600 cm^{-1}. The peaks around 1270 cm^{-1} are due to Si-O stretching vibration mode, which may be generated by the oxidation of porous silicon in the air. The peaks around 918, 763 and 680-620 cm^{-1} correspond to Si-H$_2$ scissor modes, Si-H$_2$ wagging and Si-H$_x$ (x = 1, 2, 3) bending, respectively[16,17]. It is proved that there exists Si-H bonding on the surface of porous silicon.

Spectra of composite sample prepared in the optimum condition is showed in Fig. 4(f), where three new absorption peaks appear at 1680, 1548 and 1433 cm^{-1}, respectively. The peak at 1680 cm^{-1} corresponds to O-H bending vibration mode and the peaks at 1548 and 1433 cm^{-1} are caused by N-O from NO_3^- stretching mode. Interestingly, the peak position of 1270 nm shifts to 1190 nm, implying existence of the interaction between porous silicon and Gd(NO$_3$)$_3$.

Binding energy of energy composite: Fig. 5 displays the fitted N$_{1s}$ and Si$_{2p}$ XPS results acquired from the monocrystalline silicon, fresh porous silicon and porous silicon penetrated into 0.3 nm, respectively, which all have been deposited with Gd(NO$_3$)$_3$ (for comparison). Sample (a) was used as the reference. Binding energy of N$_{1s}$ at 407.2 eV belongs to N from NO_3^-. With porous silicon penetrated, binding energy varies from 399.9-398.9 eV, indicating that -NO$_2$ might be reduced to -NH$_2$ due to the existence of Si-H$_x$. The peak at 99.5 eV is due to elemental silicon and another peak at 102.7 eV arises from Si-O. After electrochemical anodic oxidation, the two Si$_{2p}$ peaks at 101.8 and 102.3 eV correspond to SiO$_x$ ($x \geq 1$) and SiO$_x$ ($x < 1$), respectively and it is proved that the Si-H$_x$ has been oxidated to SiO$_x$ ($0.5 \leq x \leq 2$).

The contents of element in the composite are given in Table-2. The nitrogen amount at the surface is 3.25 %, but this amount decreases drastically when sample was penetrated into 0.3 nm. The same evolution is observed for the oxygen content that diminishes from 37.46-29.55 %. It is suggested that interaction between porous silicon and NO_3^- should mainly occur on the surface. Comparing with the gadolinium amount of the surface, interestingly, one in the inner increases drastically, meaning probably that Gd^{3+} squeeze into the inner. Since Gd^{3+} contains 7 unpaired electrons, it is available for the interaction between Si-H$_x$ bond and Gd^{3+} in the inner.

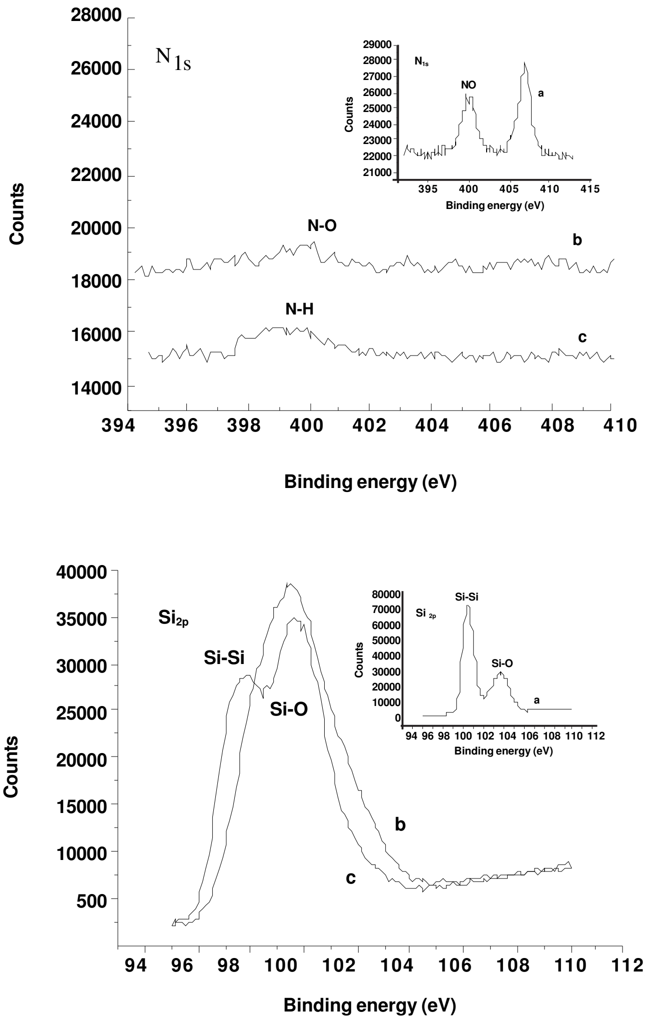

Fig. 5. Fitted N$_{1s}$ and Si$_{2p}$ XPS spectra: (a) the monocrystalline silicon; (b) freshly prepared PS; (c) PS penetrated into 0.3 nm, which all has been deposited with Gd(NO$_3$)$_3$

TABLE-2
PERCENTAGE OF ELEMENTS (%)
IN COMPOSITE BY XPS METHOD

Atom	Composite	Composite (penetrated into 0.3 nm)
O$_{1S}$	37.46	29.55
Si$_{2p}$	58.42	62.49
N$_{1s}$	3.25	0.57
Gd$_{3d}$	0.87	7.39

Conclusion

In this work, effect of electrolytes containing different HF concentrations on explosion properties was studied. When HF concentration in electrolyte is 31.4 wt %, sample is found to be optimal in terms of the explosion intensity and colour temperature. Under optimum conditions, colour temperature of the explosion is up to 3495.1 K. FT-IR spectra from porous silicon/Gd(NO$_3$)$_3$ shows that three new absorption peaks appear at 1680, 1548 and 1433 cm^{-1}, respectively. Meanwhile, binding energy of N$_{1s}$ and Si$_{2p}$ exist an obvious chemical shift. FT-IR and XPS analysis displays the existence of interaction between Gd(NO$_3$)$_3$ and Si-H$_x$ (x = 1, 2, 3) in porous silicon.

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REFERENCES

1. P. McCord, S.L. Yau and A.J. Bard, *Science*, **257**, 68 (1992).
2. D. Kovalev, V.Y. Timoshenko, N. Kunzner, E. Gross and F. Koch, *Phys. Rev. Lett*., **87**, 68301 (2001).
3. F.V. Mikulec, J.D. Kirtland and M.J. Sailor, *Adv. Mater*., **14**, 38 (2002).
4. D. Clément, J. Diener, E. Gross, N. Künzner, V.Y. Timoshenko and D. Kovalev, *Phys. Status Solidi A*, **202**, 1357 (2005).
5. E.C. Koch and D. Clément, *Propell. Explos. Pyrot*., **32**, 205 (2007).
6. M. du Plessis, *Sens. Actuators A*, **135**, 666 (2007).
7. M. du Plessis, *Phys. Status Solidi C*, **6**, 1763 (2009).
8. W. Churaman, L. Currano, A.K. Singh, U.S. Rai, M. Dubey, P. Amirtharaj and P.C. Ray, *Chem. Phys. Lett*., **464**, 198 (2008).
9. C.R. Becker, L.J. Currano, W.A. Churaman and C.R. Stoldt, *ACS Appl. Mater. Interf*., **2**, 2998 (2010).
10. Z. Li, X.L. Cheng, J. Wang and H. Chen, *Chin. J. Chem. Phys*., **23**, 281 (2010).
11. F.C. Gibson, M.L. Bowser, C.R. Summers, F.H. Scott and C.M. Mason, *J. Appl. Phys*., **29**, 628 (1958).
12. C.S. McCamy, *Color Res. Appl*., **17**, 205 (1992).
13. V. Lysenko, F. Bidault, S. Alekseev, V. Zaitsev and D. Barbier, *J. Phys. Chem. B*, **109**, 19711 (2005).
14. E.A. Petrova, K.N. Bogoslovskaya, L.A. Balagurov and G.I. Kochoradze, *Mater. Sci. Eng. B*, **69-70**, 152 (2000).
15. D.W. Cooke, B.L. Bennett, E.H. Farnum, W.L. Hults, K.E. Sickafus, J.F. Smith, J.L. Smith, T.N. Taylor, P. Tiwari and A.M. Portis, *Appl. Phys. Lett*., **68**, 1663 (1996).
16. M.A. Vásquez, G. Águila Rodríguez, García-Salgado, G. Romero Paredes and R. Penã-Sierra, *Rev. Mex. Fís*., **53**, 431 (2007).
17. J.M. Lavine, S.P. Sawan, Y.T. Shieh and A.J. Bellezza, *Appl. Phys. Lett*., **62**, 1099 (1993).