Suppressing H_2 Evolution by Silicon Powder Dispersions

S.M. Tichapondwa[a], W.W. Focke [a *], O. Del Fabbro[a], S. Mkhize[a] and E. Muller [b]

[a] Institute of Applied Materials, Department of Chemical Engineering, University of Pretoria, Lynnwood Road, Pretoria, South Africa
[b] Research and Technology, AEL Mining Services, PO Modderfontein, 1645, South Africa

Abstract

Silicon dispersions in water are used to produce pyrotechnic time delay compositions. The propensity of the silicon to react with water and to produce hazardous hydrogen gas must be suppressed. To this end the effect of surface modifications and medium pH on the rate of corrosion of silicon were studied at ambient temperature. It was found that the rate of hydrogen evolution increased with increasing pH. Silanes proved to be more effective silicon corrosion inhibitors than alcohols, with vinyl tris (2-methoxyethoxy) silane producing the best results. DTA studies were performed using a near-stoichiometric amount of lead chromate as oxidant. Comparable combustion behaviour was observed when both the fuel and the oxidant powders were either uncoated or silane modified. Mixtures of neat oxidant with silane coated silicon showed poor burn behaviour and this was attributed to poor particle-particle mixing owing to the mismatch in surface energies.

Keywords: Pyrotechnic, silicon, oxidation, water

* Corresponding author; e-mail: walter.focke@up.ac.za

Introduction

Silicon powder has found extensive use as fuel in pyrotechnic compositions [1]. Of special interest is its use in mine detonator time delay compositions [1, 2]. Such delay elements are currently manufactured by pressing pyrotechnic compositions into aluminium tubes. The automated filling and pressing process requires powders with good free flow behaviour. Spray drying of slurries is an appropriate method to obtain such free flowing granules as it creates almost perfect spherical particle agglomerates [3]. In addition to the acceptable flow properties, this process also yields well-mixed compositions from dispersions containing different powders and provides control over the agglomerate particle size distribution. The spray drying process requires that the silicon fuel and other constituents be slurried in water [3]. This creates a potential hazard situation as oxygen-containing water reacts dissociatively with silicon to form SiO_2 and hydrogen gas [4]. The overall reaction is:

Scheme I: $Si + ½O_2 + H_2O \rightarrow SiO_2 + H_2\uparrow$

The evolved hydrogen presents an explosion hazard during the production process. H_2 + air gas mixtures can support deflagration in the concentration range 4 % - 75 % (volume hydrogen fuel basis) [5].

Licciardello *et al.* [6] reported that silicon surfaces contaminated with organic compounds show significantly reduced rates of oxidation in humid environments. They attributed this effect to the hydrophobization of silicon surfaces that prevents the adsorption of water. This observation suggests that organic surface modification of the silicon powder may inhibit hydrogen evolution in aqueous dispersions.

Stroscio *et al.* [7] followed the chemical transformation of methanol on the Si (111) surface. They and Crowell *et al.* [8] found that methanol undergoes a dissociative adsorption

that proceeds readily at ambient temperatures to form a strongly-bound methoxy species (CH_3O) and SiH on the silicon surface. Salonen *et al.* [9] studied the reaction of porous silicon with water, methanol and ethanol. They found that the alcohols reacted at rates that are more than two orders of magnitude faster than the reaction with water. FTIR revealed silicon surface passivation by the formation of $Si–OCH_3$ or $Si–OC_2H_5$ groups.

Organofunctional silanes are extensively used as coupling agents for fillers and fibre reinforcements in polymer composites. They have been proposed as corrosion inhibitors for metals [10] and silicon wafers [11]. Silane coupling agents have the general structure $X – R_1 – Si – (OR_2)_3$ where $–OR_2$ represents a hydrolysable group capable of reacting with inorganic materials and R_1 is an alkyl chain that (optionally) is terminated by an organoreactive group X [10, 12, 13]. The hydrolysable part of the silane molecule is able to chemically react with hydroxyl groups present at inorganic surfaces to form a ($] – O – Si – R_1 – X$) hydrophobic barrier that prevents the transport of water to the coated surface [14]. The degree of hydrophobicity imparted by a particular silane to a coated surface naturally depends on the nature of the alkyl substituents [11].

The objective of this investigation was to find ways to inhibit hydrogen evolution by aqueous dispersions of a commercial silicon powder. The effects of pH and organic surface modification by alcohols and silanes were investigated. The effect of such surface modification on the burning behaviour of a silicon-based pyrotechnic composition was also studied by differential thermal analysis (DTA).

Experimental

Materials

Ball milled silicon Type 4 was supplied by Millrox. Middle chrome L-GXD (lead chromate) pigment was supplied by Rolfes Pigments. This pigment was used as oxidizer to test the

effect of the silane coating on the burning behaviour of the silicon. The Si + $PbCrO_4$ pyrotechnic composition was prepared using 20 wt % Si. One gram of mixture was wet mixed using a mortar and pestle with cyclohexane as a wetting agent. Some experiments used a silane coated $PbCrO_4$ sample.

The commercial silanes evaluated here are listed in Table 1. They were selected from the Silquest range produced by Momentive Performance Materials. Merck Chemicals supplied the following: absolute ethanol (99.6 %), butanol, hexanol, tetraethyl orthosilicate (TEOS), acetone and pH buffer solutions. The distilled water (pH ≈ 6) was obtained from a laboratory still.

Hydrogen evolution

Hydrogen evolution studies were performed by placing 80 g of silicon in a 500 mL flask that was immersed in a 30° C ± 1 ° C water bath. The flask was connected to an inverted graduated measuring cylinder filled with water. An aliquot of 150 mL distilled water or pH buffer solution was added to the silicon. The mixture was continuously agitated using a magnetic stirrer. The volume gas collected in the inverted cylinder was recorded at the following time intervals: 2, 5, 10, 15, 20, 30, 45, and 60 minutes. Each experiment was repeated at least five times. The moles hydrogen produced per kg Si was calculated assuming that the ideal gas law applies.

Silane coating

The amount of silane required for monolayer coverage on the silicon powder was calculated on the basis of information provided by the supplier. In all cases 25 % excess silane was added. The amounts of silane or TEOS used per kg Si Type 4 powder were: 34.3 g A1100; 36.6 g A187; 42.8 g A137; 21.0 g A1630; 23.0 g A171; 43.4 g A172, and 50 g

TEOS. The treatment solutions were prepared by combining the silane with an equal mass of distilled water and then adding ethanol to this mixture until the total mass was 100 g. To this was added 100 g of silicon powder. The slurry was stirred with a magnetic stirrer for 8 h. The solids were recovered by centrifugation, washed with acetone and left to dry in open air for one day. The amount of hydrogen evolved from the treated silicon was measured using the experimental procedure described above using distilled water as the dispersing medium. However, instead of measuring the evolved gas at different time intervals, a single reading was taken after 60 minutes.

The amount of the silane adsorbed by the silicon was determined using a modification of the procedure described by Demjen *et al.* [13]. Silane - cyclohexane solutions with different concentrations were prepared and their FTIR spectra recorded using an ATR crystal attachment. A calibration curve was established based on Beers' law. Next, 20 g silicon powder was dispersed in 50 g cyclohexane solutions containing different silane concentrations. The dispersions were stirred for 8 hours and then left to stand for a day. The liquid was decanted from the solids and the residual concentration of the silane in the cyclohexane supernatant determined by FTIR.

The silicon powder was also pretreated by stirring in ethanol, butanol or hexanol. The alcohol - silicon slurries were recovered and left to dry. The resultant powder was then tested for hydrogen evolution under the same conditions as the previous experiments, again using distilled water.

$PbCrO_4$ coated with silane A187 was prepared using the same procedure described for silicon. A 25% excess silane based on the available surface area was used, i.e. 7.11 g A187/ 100 g $PbCrO_4$.

Characterization

The particle size and specific surface area of the powders were determined on a Mastersizer Hydrosizer 2000 and a Nova 1000e BET instrument (using N_2 at 77 K) respectively. X-Ray Diffraction (XRD) analysis on a PANalytical X-pert Pro powder diffractometer was used for phase identification. The instrument featured variable divergence and receiving slits and an X'celerator detector using Fe filtered Co Kα radiation (0.17901 nm). X'Pert High Score Plus software was used for data manipulation.

Fourier Transform Infrared (FTIR) spectra of the liquids were recorded on a Perkin-Elmer Spectrum RX 1 FTIR spectrometer with an ATR attachment. The surfaces of the treated and untreated silicon's were analysed by diffuse reflectance infra-red Fourier transform analysis (DRIFT) on a Perkin-Elmer Spectrum 2000GX FTIR spectrometer. The ratio of sample mass to KBr mass was 1:20. All FTIR spectra were recorded at a resolution of 2 cm^{-1} and represent the average of 30 scans.

X-Ray Photo-electron Spectroscopy (XPS) spectra were obtained on a Quantum2000 Physical Electronics spectrometer equipped with an Mg/Al dual mode source and a small area analyzer with PSD detector. An achromatic Al Kα X-Ray (1486 eV) source was operated at 20 W. The vacuum pressure was 10^{-8} torr during spectra acquisition. Survey spectra were obtained at take-off angles of 15º, 45º and 80º. Before analysis, samples were dried over P_2O_5 in a vacuum desiccator.

Differential thermal analysis (DTA) was carried out on a Shimadzu DTA-50 instrument. Approximately 5 mg of the sample and standard (α-Al_2O_3) where weighed into alumina sample pans. Ca. 500 µm thick copper disks were placed at the bottom of the sample pans. These acted as heat sinks to protect the DTA temperature detector from large temperature excursions. The DTA test runs where carried out in a nitrogen atmosphere and the temperature was scanned from ambient to 1000 °C at a rate of 50 °C/min.

Thermogravimetric Analysis (TGA) of treated and untreated silicon was performed using the dynamic method on a Mettler Toledo A851 TGA/SDTA instrument. About 15 mg powder was placed in open 70 μL alumina pans. Temperature was scanned from 25 to 1000 °C at a rate of 10 °C/min with air flowing at a rate of 50 mL/min.

Results

Powder and surface characterization

The silicon Type 4 powder was found to have a d_{50} particle size of 2.06 μm and a specific surface area was 9.7 m^2/g. The lead chromate ($PbCrO_4$) d_{50} particle size was 2.14 μm and the BET surface area was 16.7 m^2/g. XRD analysis confirmed that the silicon was crystallographically pure.

Fig. 1 shows DRIFT spectra for neat silicon and silicon powders exposed to hexane solutions containing 10% A172 and 14% A1100 respectively. Consider first the spectrum obtained for the neat silicon. The band at 3400 cm^{-1} is attributed to O–H stretch vibrations of the Si–OH groups. The band at 1000 – 1200 cm^{-1} represents the asymmetric stretch vibration of Si–O–Si bonds. The presence of this band confirms the existence of SiO_2 at the surface of the silicon powder. The peak at 1600 cm^{-1} indicates the presence of water or O–H bonds at the surface [4]. The bands observed at 3000 – 2700 cm^{-1} reveal the existence of organic alkyl groups. Their presence in the spectrum of the neat powder implies organic contamination of the neat silicon surface. However, there are clear differences between these bands in the spectra for the neat silicon and those for the silane treated samples. This suggests that the nature of the organic present at the silicon surface had changed. The spectra reported for the two treated samples in Fig. 1 also differ. This is expected as the two silanes featured different functional groups. Unfortunately, the C = C stretch band and the band for N–H bending of the

silane molecules overlap with the range for the O–H band observed for the silicon powder. This made it difficult to accurately allocate the peaks.

XPS has been used as a characterization technique in various surface modification studies [15]. The technique samples the composition of matter at a surface depth of a few nanometres. The XPS-determined elemental surface concentrations for the neat silicon and silane-coated silicon's are compared in Table 2. The results for the neat silicon indicate 18.2 % carbon and this confirms the presence of the organic contamination first revealed by DRIFT. The silane-coated materials showed higher carbon contents and decreased silicon contents indicating surface alterations due to organic coating. The presence of the organic coating was additionally confirmed for silane A1100. In this case the unique nitrogen component was detected on the silicon surface by XPS.

The dissolution experiments showed that the actual amount of silane adsorbed on the silicon surface was independent of the initial silane content of the hexane solutions that the silicon powders were exposed to. The average amount of silane adsorbed for the six different silane concentrations considered were found to be 35 g A172 silane/kg silicon and 84 g A1100 silane/kg silicon. The results obtained for A172 were in agreement with the theoretical quantity based on molecule surface coverage and the measured surface area of the silicon. However, the experimentally determined amount for A1100 significantly exceeded the theoretically expected coverage. This discrepancy might have been caused by multilayer silane deposition on the silicon powder surface.

TGA analysis was also used to estimate the amount of silane actually bound to the silicon (Fig. 2). The neat silicon showed no significant mass loss in the range 25 °C to 600 °C. Instead, above 600 °C, it showed a mass increase associated with the formation of silicon nitride. The A172 silane coated silicon showed a maximum mass loss of 1.62 % between 25 - 800 °C. This mass loss exceeded that expected from the dissolution experiments. Corrections

where made to the dissolution data to take into account that only the organic component of the bound silane will vaporise upon heating. The expected mass loss, based on the vaporisation of the organic component of the silane, was 4.35% for A1100-coated silicon. This compares favourably with the maximum observed TG-mass loss of 4.55 % observed above 150 °C. Note that this powder also showed a mass loss of 2.63 % between ambient and 125 °C owing to the loss of moisture and possibly some unbound excess silane.

Effect of pH on H_2 Evolution

The hydrogen release measurements showed considerable scatter. Fig. 3 shows representative curves that correspond to an average of at least five different runs. In the series pH = 2 buffer, distilled water (pH ≈ 6) and a pH = 10 buffer solution, the rate of H_2 evolution increased with pH. In each case the apparent release rate also decreased over time. Metal oxidation rates are usually expressed either in terms of the mass gain or the increase in the thickness of the oxide layer. The Deal-Grove linear parabolic oxide growth law applies when this growth is diffusion limited [16]. If the oxidation reaction involves water only, the amount of hydrogen evolved should be proportional to the amount of oxide formed. In this case the parabolic law can be expressed as follows:

$$N_{H_2} = a\sqrt{(t+b)} - a\sqrt{b} \qquad (1)$$

where N_{H_2} is the moles H_2 released per unit mass of silicon and *a* and *b* are empirical constants. Gräf *et al.* [17] found that the oxidation of HF etched silicon in water follows the so-called "logarithmic law". Expressed in terms of the amount of hydrogen gas evolved it reads:

$$N_{H_2} = a\ell n(t+b) - a\ell nb \qquad (2)$$

This equation provided a better fit to the present data and this is indicated by the solid lines in Fig. 3. However, an unequivocal conclusion in this regard is not possible due to the considerable scatter in the data.

Effect of alcohols and silane treatments on H_2 evolution

Fig. 4 shows the amount of hydrogen evolved after a one-hour submersion of surface treated silicon powder in distilled water. The neat, i.e. uncoated silicon powder produced 8.3 ± 1.2 mmol H_2/kg Si. Both the alcohols and the silanes treated silicon powders reduced the amount of H_2 gas produced. TEOS was not very useful as its performance was in the range found for the alcohols. However, the silanes were significantly more effective. The best performance was 0.25 ± 0.50 mmol H_2/kg Si obtained with Silquest A172, i.e. vinyl tris(2-methoxyethoxy) silane. The worst silane result was 1.47 ± 0.06 mmol H_2/kg Si provided by Silquest A187 (γ-glycidoxypropyl triethoxysilane). This still represents a reduction of 83 % in the amount of H_2 released over a period of one hour. The performance of the other silanes tested here was comparable. Surprisingly this group included octyl triethoxysilane (Silquest A137). It features the longest alkyl chain and, besides, there is no substituent present at the end of this tail. So it was actually expected to provide the best effect with respect to imparting hydrophobicity to the silicon surface. Silquest A172 and A171 share the same vinyl substituent but differ with respect to the alkoxy groups. In the former the hydrolysable group comprises the 2-methoxyethoxy rather than the more commonly employed methoxy functionality present in Silquest A171.

DTA burning behaviour

The pyrotechnic composition of silicon and lead chromate ($PbCrO_4$) was used to establish the effect of silane coating on the DTA response of the composition. The DTA response is shown in Fig 5. The untreated silicon gives a sharp exothermic peak with an ignition temperature of about 660°C. The two silane coated silicon compositions show weaker exotherms with an ignition temperature of around 690 °C. The presence of silane coatings apparently decreased the reactivity of the silicon as characterized by DTA measurements. Berger [18] states that the particle size, the active surface of the oxidizer or the fuel, and the degree of mixing are the parameters influencing pyrotechnic reaction rates. It is unlikely that the first two factors were changed by the silane treatment. The most likely explanation is that a poorly mixed composition was obtained when the hydrophobic silane coated sample was processed with the neat, hydrophilic oxidizer. Support for this contention is provided by the results obtained for the composition containing A172 coated silicon and A187 coated $PbCrO_4$. It produced the sharpest exotherm, sharper than the composition comprising the untreated compounds. This means that the presence of the silane coatings *per se*, was not responsible for the impairment of the burning behaviour when uncoated oxidizer was used.

Discussion

The theoretical amount of hydrogen gas evolved was calculated considering the face centred cubic unit cell structure of silicon crystals [19]. It was assumed that the Si was initially not oxidized and that exactly one layer of Si reacts to form SiO_2. The amount of hydrogen produced with these assumptions was estimated as 332 mmol H_2/kg Si. The Si exposed to water for 1 hour produced an average of 8.3 mmol H_2/kg Si. This implies that the approximate amount of surface Si available for reaction in the present experiments was only about 2.5 % of that of a pure silicon surface.

Corrosion of metals is usually electrochemical in nature. That means that chemical reactions operate in which transfer of electrons from one species to another occurs. At anodic regions the metal atoms undergo oxidation reactions in which they give up electrons. The electrons generated are transferred to cathodic regions where they take part in cathodic reactions with another chemical species. Silicon is not metallic but rather a semiconductor and is reported to be one of the most powerful non-metallic reducing agent [20]. Its corrosion in aerated neutral to slightly basic aqueous media can be described in electrochemical terms [21]. Two possible half reactions are shown in Scheme II. Note that the holes, labelled h^+, are annihilated at the silicon anode and this is equivalent to generation of electrons e^- at the interface.

Anode: $Si + 2\ OH^- + 2\ h^+ \rightarrow SiO_2 + H_2\uparrow$

Cathode: $½\ O_2 + H_2O + 2\ e^- \rightarrow 2\ OH^-$

Overall: $Si + ½O_2 + H_2O \rightarrow SiO_2 + H_2\uparrow$

Scheme II. Electrochemical model for the oxidation of silicon in neutral aqueous medium [21].

The half reactions in Scheme II are not necessarily primitive reactions. Gräf *et al.* [17] postulated that silicon corrosion is initiated by the formation of Si–H functional groups. They also posited that the subsequent reaction with hydroxyl ions and conversion to Si–OH represents the rate limiting reaction. Their proposed mechanism also provides a plausible explanation for the corrosion of neat silicon in water. The silicon powder already featured oxygen atoms that are chemically bonded to surface silicon atoms. Since oxygen is decidedly more electronegative than silicon, these bonds are polar in nature with the silicon atom featuring a net positive charge (δ^+). This charge induces a net negative charge in a neighbouring silicon atom (δ^-) which, in turn, induces a net positive charge (δ^+) to its

neighbour. According to Gräf *et al.* [17] this induced polarization enables a H_2O molecule to attack the polarized Si–Si bond:

$$Si^{\delta+}–Si^{\delta-} + H_2O \rightarrow Si–H + Si–OH$$

Ultimately Si–O–Si bridges are formed by the condensation of neighbouring Si–OH groups:

$$Si–OH + Si–OH \rightarrow Si–O–Si + H_2O$$

Gräf *et al.* [17] assumed slow conversion of Si–H to Si–OH. This revised anodic reaction involves nucleophilic attack of OH^- ions on Si–H bonds and releases hydrogen that is evolved as a gas:

$$2\ Si–H + 2\ OH^- + 2\ h^+ \rightarrow 2\ Si–OH + H_2\uparrow$$

The partial dissociation of Si–OH into $SiO^- + H^+$ leads to a charging of the interface and generates a surface potential. Gräf *et al.* [17] took this into account and showed that, with the additional assumption that the Si–H concentration remains approximately constant, that

$$\frac{d[\text{Si-OH}]}{dt} \propto e^{-c[\text{Si-OH}]/RT} \tag{3}$$

where c is a constant describing the dissociative behaviour of Si-OH. According to Gräf *et al.* [17] this primitive anodic reaction is rate limiting and it therefore determines the overall kinetics of hydrogen evolution. Integration of equation (3) yields the logarithmic growth law of equation (2).

Conclusions

The oxidation of silicon powder in water was studied and the effects of medium pH and surface modifications on the rate were investigated. Hydrogen evolution kinetics of unmodified silicon submerged in buffer solutions appeared to follow the logarithmic rate law. It was found that silane coupling agents are effective short-term inhibitors of silicon corrosion in water and that approximately a monolayer attaches to the silicon despite the

presence of an organic contaminant. Vinyl tris(2-methoxyethoxy) silane was identified as the most effective inhibitor. The present data also hints at the possibility that the nature of the hydrolysable group may affect the corrosion inhibition performance of the silane with respect to silicon exposed to water. DTA evaluations indicate that employment of a silane coating on the silicon fuel necessitates a corresponding surface treatment of the oxidizer powder to ensure that intimate mixing of the reagents is achieved.

Acknowledgements

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Table Captions

Table 1. Commercial silanes used for the surface treatment of the silicon powder.

Table 2. XPS results for surface properties of neat silicon and silane-treated silicon powders.

Figures Captions

Figure 1. DRIFT spectra of neat silicon and silicon powders treated with ethanol solutions of silanes (10% A172 or 14% A1100).

Figure 2. TG mass loss of neat and silane treated silicon in a nitrogen atmosphere.

Figure 3. Effect of pH on the hydrogen evolution rate from neat silicon powder dispersions. The solid lines represent "logarithmic rate law" fits according to Equation (2).

Figure 4. Amount of hydrogen gas produced after one hour of exposure to distilled water for alcohol-treated or silane-coated silicon powders.

Figure 5. DTA characterization of the 20 wt % Si – 80 wt % $PbCrO_4$ pyrotechnic compositions in a nitrogen atmosphere and at a temperature scan rate of 50 °C/min. (a) A172 treated Si + A187 treated $PbCrO_4$ (b) Si + $PbCrO_4$ (c) A1100 treated Si + $PbCrO_4$ (d) A172 treated Si + $PbCrO_4$.

Table 1. Commercial silanes used for the surface treatment of the silicon powder

Silane	(Silquest code)	Surface coverage* (m^2/g)
γ-aminopropyltriethoxysilane	(A1100)	353
γ-glycidoxypropyl triethoxysilane	(A187)	330
Octyl triethoxysilane	(A137)	283
Methyl trimethoxylsilane	(A1630)	575
Vinyl trimethoxysilane	(A171)	527
Vinyl tris(2-methoxyethoxy)silane	(A172)	279

*Surface area coverage data supplied by manufacturer

Table 2. XPS results for surface properties of neat silicon and silane-treated silicon powders.

Element	**Atomic concentration (wt %)**		
Silicon	Neat	A172	A1100
C	18.2	28.0	23.0
O	43.3	40.3	41.9
Si	38.5	31.7	32.5
N	-	-	2.6

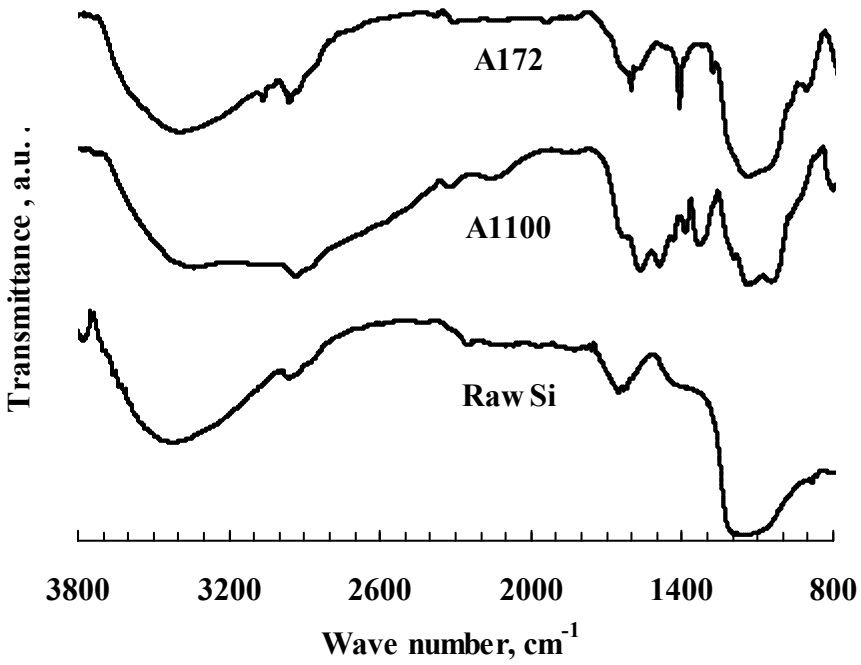

Figure. 1. DRIFT spectra of neat silicon and silicon powders treated with ethanol solutions of silanes (10% A172 or 14% A1100).

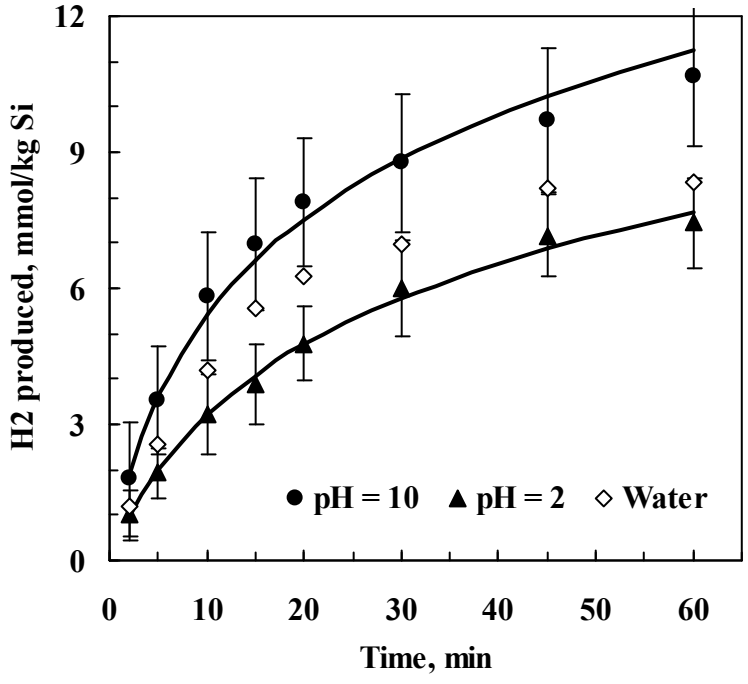

Figure 2. Variation of hydrogen evolution rate with pH fitted with the "logarithmic rate law" shown in equation (2).

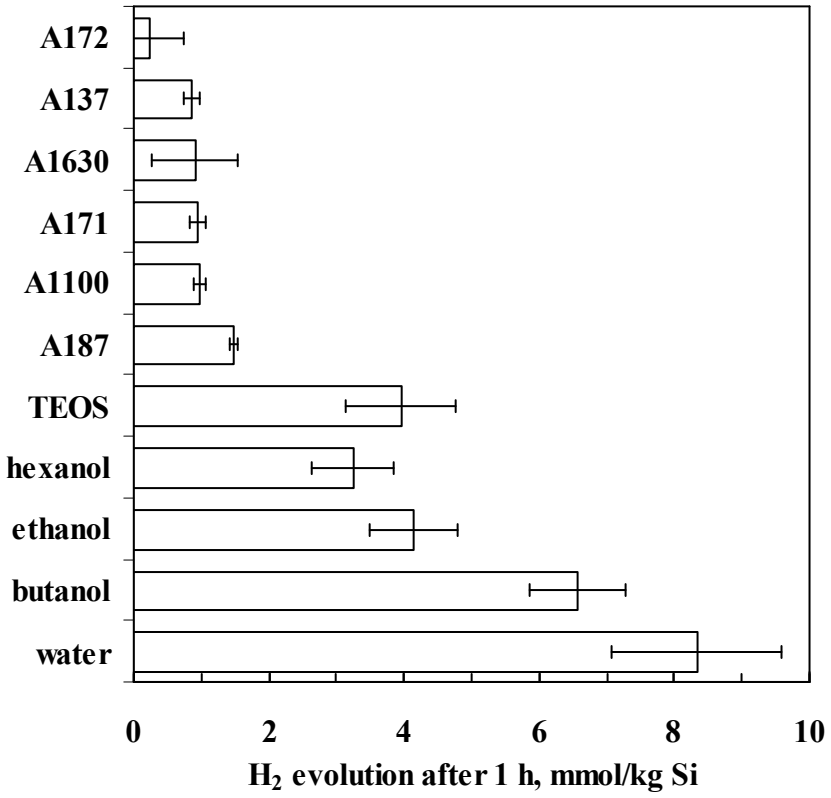

Figure. 3. Amount of hydrogen gas produced from alcohol treated or silane coated silicon powders submersed in distilled water for 1 hour.

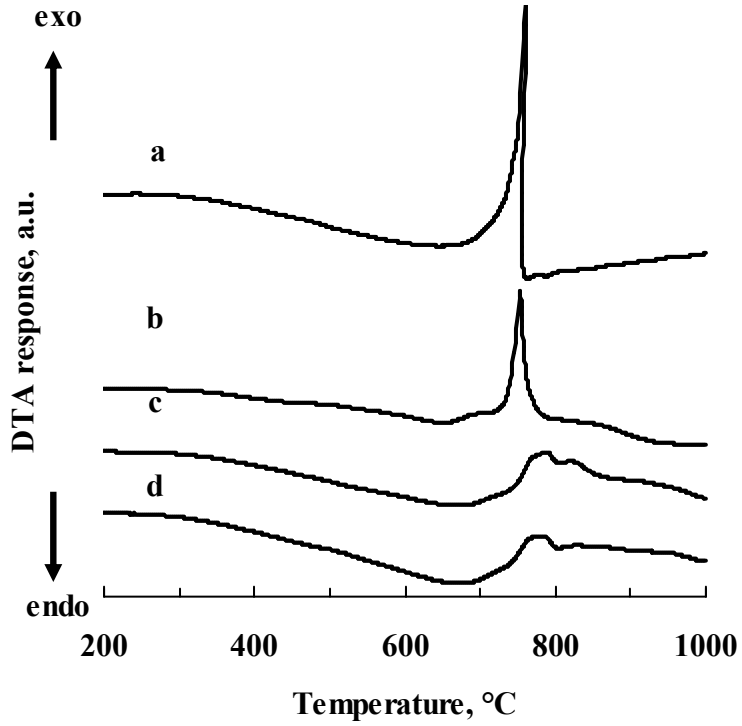

Figure 4. DTA characterization of the 20 wt % Si – 80 wt % $PbCrO_4$ pyrotechnic compositions in a nitrogen atmosphere and at a temperature scan rate of 50 °C/min. (a) A172 Si + A187 $PbCrO_4$ (b) Si + $PbCrO_4$ (c) A1100 Si + $PbCrO_4$ (d) A172 Si + $PbCrO_4$

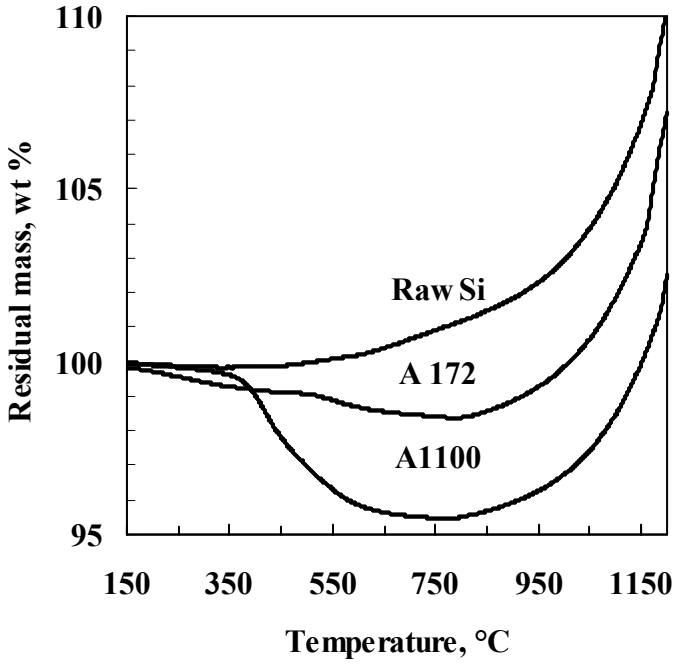

Figure. 5. Mass loss of untreated and silane treated silicon in nitrogen atmosphere