Evaporation and decomposition of acrylic acid grafted luminescent silicon quantum dots in ultrahigh vacuum

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Abstract. A thin film of silicon quantum dots (Si-QDs) is a potential thermoelectric material with a high figure of merit. Evaporation and deposition in ultrahigh vacuum is a novel method to produce such a thin film of high quality. Acrylic acid grafted luminescent Si-QDs have been synthesized by a simplified method. Their surface electronic core levels were investigated by X-ray photoelectron spectroscopy (XPS) at various temperatures. At room temperature, three components at 100.4, 102, and 104.4 eV were identified, corresponding to Si core, Si-C, and silicon oxide on surface, respectively. The appearance of Si-C component showed that acrylic acid has been successfully grafted onto Si-QDs surface. At 200°C, intact evaporation took place and the ratios of silicon to carbon in core levels remained constant as the annealing time increased. Decomposition occurred at 340°C, where the ratios of Si₂p to C₁s began to change. The XPS results are in agreement with thermogravimetric analysis (TGA) measurements which showed a sharp weight loss of 80% at 200°C, which is the intact evaporation temperature. Another slow weight loss of 14% took place between 300°C and 500°C, which is a footprint of surface Si-C decomposition.

1. Introduction

Owing to its electronic and optical properties, functionalised Si-QDs have attracted enormous interest in the past decades [1-7]. Since smaller QDs were preferred to evaporate at lower temperatures, the intact evaporation of quantum dots could provide a unique method to process thin films of size-selected functionalised QDs [8], which could open the door for applications in memory devices and thermoelectric modules. With the conventional oxide layer replaced by Si-QDs in memory devices, the retention time and lifetime of the devices will be enhanced enormously [9, 10]. Since the nanostructured silicon size would be smaller than the phonon mean free path, the thermal conductivity would be reduced by 100 fold [1, 2]. Such thin films of Si-QDs could be next generation of energy materials converting waste heat or solar energy to electricity. Owing to phonon blockage the QDs with low thermal conductivity could possess high figure of merit thus convert thermal energy to electricity more efficiently. Furthermore, current resources of thermoelectric materials, such as Bi₂Te₃ and PbTe, are running out rapidly. Silicon is one of the most abundant resources on the earth, is non-toxic and ecologically friendly. If it could be used to replace current thermoelectric materials, it would mark a significant breakthrough in fundamental sciences and energy conversion technologies.

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QDs have been used as fluorescent labels for bio-molecules. They could be future alternatives to the traditional organic dyes in case of bio-imaging [7, 11-13]. Moreover, QDs have several advantages over the traditional organic dyes [7]: resistance to photobleaching which permits the QDs to be imaged for a longer period to time devoid of any loss of luminescence; QDs could be designed with an emission range from the visible to the IR region; they have narrow, symmetrical emission peaks and a broad absorbance band; relatively high quantum yields; different QDs of different emission characteristics can be excited simultaneously at a single wavelength; and QDs are 20 times bright than traditional organic dyes. Since Si-QDs surface can be modified with water dispersible ligands, and they emit visible red light, water dispersible Si-QDs are desired by biological and medical applications. Acrylic acid grafted luminescent Si-QDs are among bio-compatible quantum dots that are water dispersible, non-toxic, and emitting bright red light [14-16]. Therefore their thermal stability with temperatures is important for future applications.

The evaporation and decomposition of alkylated Si-QDs has been investigated [8], but such a study on acrylic acid grafted Si-QDs remains to be performed. Here we report an XPS study on the evaporation and decomposition of acrylic acid grafted Si-QDs, with confirmation via TGA results. This is the first report comparing the XPS results with TGA analysis and proved these results are in agreement.

2. Experimental
The simplified method of synthesising acrylic acid grafted luminescent Si-QDs has been published elsewhere [14]; here we provide a brief description of the sample preparation. Photoluminescent silicon layers were formed by galvanostatic anodisation of boron-doped p-Si (100) oriented wafer (10 Ω·cm resistivity, Compart Technology, Peterborough, UK) in a 1:1 v/v solution of 48% aqueous hydrofluoric acid (HF) and ethanol solution. The circular electrochemical etching cell (1 cm diameter) was machined from polytetrafluoroethylene (PTFE). The silicon wafer was sealed to the base using a Viton™ O-ring. The counter electrode was a piece of platinum wire coiled into loop to improve the uniformity of the current distribution, and the etching was carried out using KEITHLEY 2601 in constant current source mode. A layer of luminescent porous silicon was made at high current density (5 minutes at 550 mA/cm²). The solution was decanted and the fluorescing porous silicon layer on the chip was transferred to a Schlenk flask and dried under the vacuum of a rotary pump for 2 hours. The air within a 1:99 v/v solution of acrylic acid and ethanol aqueous was purged by N₂ bubbling for 2 hours. The solution was then added to the Schlenk flask containing Si chips (working under N₂ protection.) The Schlenk flask was tightly closed and subjected to ultrasonic dispersion for 50 minutes at 40 °C. The mixture was then poured into a polyethylene bottle and treated with N₂ bubbling for 10 minutes to purge the air. Afterwards the mixture was inserted into an UV reactor and stirred at 50 °C for 5 h. This procedure changes the Si-QDs surface termination from hydrogen (H-) to poly acrylic acid(PAA-) group. After filtration the luminescent solution was collected. A photoluminescence (PL) spectrum was acquired with a PerkinElmer LS55 Fluorescence Spectrometer with the excitation from

![Figure 1. Solid line: PL emission spectrum from PAAc grafted Si-QDs with UV excitation wavelength 250 nm and filter at 290 nm. The main peak position is at 610 nm and the minor peak at 403 nm; dash line: excitation spectrum at emission 610 nm, the peak wavelength is at 378 nm.](image-url)
a Xenon lamp at 250 nm and a filter at 290 nm. The excitation spectrum was obtained by collecting the emission at 610 nm.

A few drops of the prepared sample were cast onto a gold foil substrate prior to insertion inside the XPS system preparation chamber. High resolution XPS core level measurements were performed with a Scienta ECSA300 at NCESS, Daresbury Laboratory. Evaporation and decomposition experiments were carried out in a VG Escalab 250 in LENNF, Leeds University, equipped with a conventional hemispherical sector analyser and controlled by a VGX900 data system. XPS experiments were carried out using a high intensity monochromated Al Kα source (1486.6 eV) operated at 15 kV and 20 mA. O1s, C1s and Si2p spectra were recorded using a pass energy of 20 eV. The energy scale of the spectrometer was calibrated to the Ag 3d5/2 peak at 368.3 eV. The binding energy scale was calibrated to the Au4f7/2 at 84.0 eV. High-resolution peak fitting was performed using the manufacturers’ software.

Thermogravimetric analysis (TGA) was performed with a METTLER TOLEDO TGA system from ambient environment conditions up to 650°C, with the rate of temperature increase set at 20°C per minute and using a 40 µl aluminium pan under dry nitrogen gas flow protection.

3. Results and discussion:

Figure 2. XPS core levels at room temperature in region (a) Si2p, (b) C1s, and (c) O1s. The Si2p was fitted with a Shirley background and three doublets to demonstrate there are different species on Si-QDs surface. Three components at 100.4, 102, and 104.4 eV, respectively, were ascribed to Si core, Si-C, and Si-O related species.
The prepared samples show a strong luminescent emission at peak 610 nm (orange), equivalent to 2.03 eV, and the excitation spectrum shows a peak at 378 nm (or 3.28eV), see figure 1. The separation between these peaks is 232 nm (or 1.25 eV). There are two mechanisms proposed for PL from Si-QDs [17]: one is sized effect based quantum confinement model, i.e. the excitation process occurs between the quantized levels of QDs, and subsequent radiative recombination processes may take place directly via these levels [18, 19], or alternatively via surface/interfacial states [20, 21]; another mechanism is due to particular species irrelevant to the quantum dots, i.e. both the processes take place in certain kind of species (e.g. a surface-bound oxyhydride-like emitter or SiOx-related defects act as luminescent centres like those found in a-SiO2) [22-25]. The orange peak from our acrylic acid grafted Si-QDs follows the first mechanism proposed above. Based on the calculation by Wolkin [21], this indicates the size of Si-QDs to be approximately 5 nm in diameter, which is in consistent with our previous DLS, HRTEM and AFM results [14]. The minor peak at 403 nm (blue) is attributable to Si-O related species following the second mechanism above. PL bands located in near ranges have been found in a-Si:H:O films formed by CVD and Si+ implanted SiO2 films [23, 26].

That Si-O species exist on the Si-QDs surface can be demonstrated by the XPS core level spectra. Figure 2(a) shows a core level spectrum at room temperature in Si2p region, which can be fitted with a Shirley background and three doublets. Three components at 100.4, 102, and 104.4 eV, respectively, are ascribed to Si core, Si-C, and Si-O related species. Since the QDs were grafted by acrylic acid, Si-C species was the majority in this fitting. This is similar to the results from alkylated Si-QDs [27]. The core levels at room temperature in C1s and O1s regions, shown in figure 2(b) and (c), confirmed the possibility of existence of Si-C and Si-O related species.

![Figure 2](image_url)

**Figure 2.** The analysis of ratio of Si:C in the core level spectra at different annealing temperatures over a series of annealing times: (a) 200°C; (b) 340°C. The results show that there is no significant Si:C ratio change when the samples were annealed for 1, 3, 6, 11, 21, 51, and 81min at 200°C, which is the intact evaporation temperature; when samples were annealed at 340°C, the ratio of Si:C increased with annealing time, owing to decomposition at this temperature.

In 2007 it was unveiled that evaporation of intact alkylated Si-QDs in UHV at relatively low temperature of ~ 200°C, compared to the normal silicon boiling point of 1414°C [8]. The intact sublimation is enabled by a combination of anomalously weak inter-particle interactions and the extremely high thermal stability of the alkyl-coated silicon nanoparticles. Hence, the exploration of the evaporation behaviour of acrylic acid grafted Si-QDs in vacuum is interesting. The measurements were carried out by monitoring the Si2p and C1s core levels over several annealing cycles of of 1, 3, 6, 11, 21, 51, and 81 minutes at 200°C, which is the temperature at which they are expected to evaporate intact. The results (figure 3a) show that there is no significant Si: C ratio change. The constant ratio of Si to C implies that the PAAc Si-QDs evaporated intact without undergoing decomposition. It is worth noting the desorbing temperature for non-covalently anchored monolayers such as the alkanethiol self-
assembled monolayers is about 175 °C [28]. This proves that the carboxyl groups were covalently anchored to Si-QDs surface, which is consistent with the core level Si2p at room temperature which showed the existence of Si-C component.

Interestingly, once the samples were annealed at 340°C, the ratio of Si to C rose (figure 3b). At this temperature it is believed that decomposition of the covalent anchored monolayer on Si took place [29]. Decomposed carboxyl groups from Si-QDs surface were burned and pumped away in UHV, thus the Si:C ratio rose.

To investigate the thermal properties of poly acrylic acid grafted Si-QDs further, TGA analyses were carried out with dry samples. Figure 4 shows a scan from the ambient environment to 650°C under the protection of dry nitrogen gas flow at 20°C per minute temperature rate using 40 µl aluminium pan: a sharp weight loss, 80%, at 200°C which is intact evaporation temperature; further 14% weight lost between 300°C and 500°C during the decomposition.

4. Conclusions:
Acrylic acid grafted luminescent Si-QDs were synthesized by a simplified method. Their surface electronic core levels were investigated by XPS at various temperatures. At room temperature, the core level in Si2p region was fitted with three doublets and a Shirley background. Three components at 100.4, 102, and 104.4 eV were corresponding to the Si core, Si-C, and silicon oxide on the surface, respectively. The appearance of a Si-C component shows that acrylic acid had been successfully grafted onto the Si-QDs surface. At 200°C, the Si-QDs evaporated intact and the ratios of silicon to carbon core levels were constant with the increasing annealing time. Decomposition at 340°C was observed with the change in Si2p to C1s ratio with the annealing time. The XPS results were in agreement with TGA. TGA measurement showed a sharp weight loss of 80% at 200°C which is the intact evaporation temperature. Another slow weight loss happened between 300°C and 500°C, a further loss of 14% weight, which is a footprint of surface Si-C decomposition.

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