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Luminescent colloidal silicon particles

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Received 25 January 1994; in final form 25 February 1994

Abstract

Crystalline silicon particles, which are coated by an oxide layer, are prepared by combustion of silane. Red or orange luminescence is activated by etching them in a 1:1 cyclohexane–propanol-2 suspension by aqueous hydrogen fluoride in the presence of air. The temporal changes in the luminescence intensity of the suspension (several days) are described. When a suspension of luminescent particles in cyclohexane is mixed with polar solvents such as alcohol, ether and chloroform, a more or less quenching of the luminescence (depending on the nature of the added solvent) occurs. Mixing with non-polar solvent such as carbon tetrachloride does not lead to quenching. Triethylamine and ammonia quench the luminescence extremely effectively. Sulfuric acid also quenches. The particles migrate in an electric field in different directions depending on the chemical surface treatment. It is concluded that luminescence occurs when the particles carry only a few oxidized centers on the surface, and the protonation state of these centers strongly affects the luminescence.

1. Introduction

The combustion of silane under oxygen-deficient conditions leads to a powder of crystalline silicon particles which are covered by an oxide layer. The particles can to a large extent be dissolved in water to yield a colloidal solution. Illumination of the solution with UV light leads to the oxidation of the silicon particles [1]. In the present report, a method is described to activate the luminescence of these particles. The luminescence of Si particles has to be seen in close context to the luminescence of porous silicon where various mechanisms have been proposed such as size quantization [2], surface state effects [3] and the effects of siloxanes [4].

The preparation of luminescent silicon particles in colloidal suspension has previously been achieved by two methods: (1) Brus and co-workers produced crystalline Si particles by thermal decomposition of disilane in a helium stream, oxidized them in the stream, collected them in ethylene glycol, and activated the luminescence by boiling at 200°C after the addition of sulfuric acid, pH = 1 [5]. (2) We have reported on crystalline Si particles formed in the laser-induced plasma of an argon–silane mixture [6]. These particles could be suspended in a solvent and their luminescence activated by etching with hydrogen fluoride.

The etching method is also applied in the present study. The luminescent particles were suspended in cyclohexane, a non-polar solvent, and the quenching of the luminescence by added substances of different polarity and acid-base properties was investigated.

2. Experimental results

The combustion of SiH_4 occurred in a 50 ml syringe as described previously [1]. (The precautions which have to be taken are also described in ref. [1].)

The syringe was flushed with argon and then filled with 10 ml silane, and 10 ml air was allowed to enter by slowly withdrawing the plunger. The powder, which was deposited on the wall inside the syringe, was suspended in a 1:1 mixture of cyclohexane and propanol-2 by soaking 30 ml of this mixture into the syringe, and by subsequent violent shaking and exposing the suspension to ultrasound. The total amount of suspended powder was 7 mg. This material does not luminesce.

Fig. 1 illustrates the various steps (A) to (D) of the etching procedure. (A) The content of the syringe is transferred to a 100 ml teflon bottle. (B) 5 ml aqueous HF (40%) is added and the solution shaken. Two liquid phases are formed. The upper phase mainly consists of cyclohexane, although HF in a small concentration will also be present in this phase. (C) The particles move into the upper phase. This can be followed by recording the absorption spectrum of the upper phase at various times of ageing. As can be seen from the upper part of Fig. 2, the spectrum becomes more intense during the first two hours. At this point, luminescence has not yet developed. Upon further ageing, the absorption spectrum decreases in intensity (lower part, Fig. 2) and the luminescence develops, the color of the emitted light being red in the beginning and then turning to orange. Every six hours the flask was treated in an ultrasonic bath for 1 min and stirred for 30 min. (D) Upon further ageing, the orange luminescence decreases in intensity. During all these steps, the system stands in air. When the experiment is carried out under argon, no noticeable luminescence develops. It should also be noticed that the amount of HF in the system is much larger than that of silicon. As can also be seen from Fig. 2 (lower part) the shape of the spectrum changes at long times (60 h) which might be taken as an indication of a change in the electronic structure of the particles (possibly by strong size quantization as they become very small).

Fig. 3 shows luminescence spectra of the upper phase at various times of ageing. 1 ml of the upper phase was added to 9 ml cyclohexane, and the luminescence measured in a commercial fluorimeter (Spex, type Fluoromax TM). One can see how the absorption maximum shifts to shorter wavelengths with increasing ageing time. The quantum yield is given on the curves. It increases with time to reach 7% at 60 h. Upon further ageing there is no more blue-shift but the orange luminescence fades away.

The decay in the intensity of the red and orange luminescence was not observed when the material was recovered in the solid state: 1 ml of the upper phase was dissolved in 9 ml cyclohexane, the solution centrifuged (laboratory centrifuge, 4000 rot/min) and the liquid decanted. The sedimented material was again suspended in 9 ml cyclohexane, sedimented by centrifugation and dried. This procedure was carried out to remove traces of impurities, such as water and HF, from the cyclohexane phase. The dried material still emitted several weeks after the preparation. The
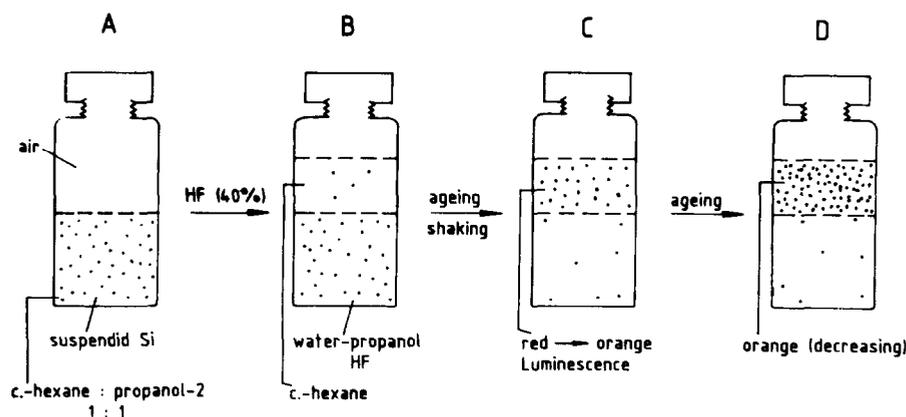

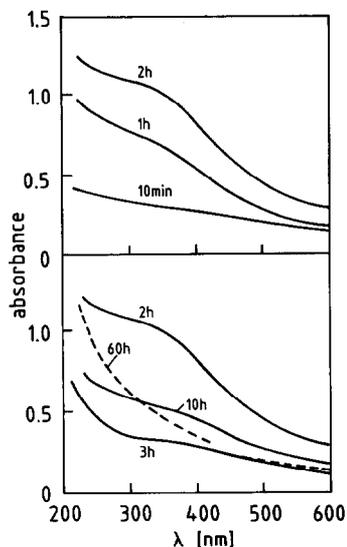Fig. 1. Schematic description of the various steps of the etching procedure.

Fig. 2. Absorption spectrum of the upper phase (Fig. 1) at different times of ageing. To measure the spectrum, 1 ml of the upper phase was taken at various times and diluted with 9 ml cyclohexane.
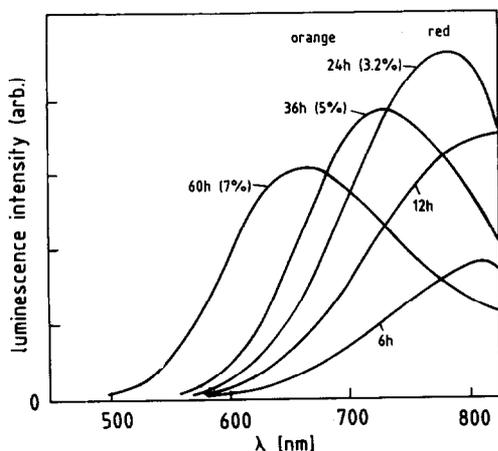

Fig. 3. Luminescence spectra of the upper non-polar phase at various times of ageing (——). Excitation wavelength: 360 nm. The numbers in parentheses give the quantum yield of luminescence. It was determined by comparing the area of the luminescence band with that of rhodamine 6G which is known to fluoresce with a quantum yield of 100%.

solid material can also be inserted in a matrix, for example, of polymethylacrylate.

Electron microscopy showed that the particles in the red luminescing solution had mainly diameters around 100 Å. As the luminescence color moved towards orange, mainly particles in the size range from

40 to 60 Å were seen. When the luminescence faded away ((D) in Fig. 1), mainly particles of 20 Å and smaller sizes were present.

In the luminescence-quenching experiments, a sample of the upper phase ((C) in Fig. 1) was purified by twofold sedimentation and suspension in cyclohexane as described. The concentration of the material in the purified suspension was less than 0.5 mg/10 ml. Despite this low concentration, the solution luminesced brightly. Various amounts of quenching substances were added and the luminescence spectrum was recorded. In Fig. 4, the intensity in the maximum of the luminescence band is plotted as a function of the volume fraction of various added liquids. The luminescence intensity is corrected for the dilution which was brought about by the addition of the second liquid. It can be seen that all the added solvents quench the luminescence with the exception of carbon tetrachloride where even an increase in intensity is observed. It is interesting to note that all the quenching solvents are polar whereas cyclohexane and carbon tetrachloride, the two solvents in which the particle luminesce strongly, are non-polar. With increasing concentration of the quenching solvent, the band maximum is slightly blue-shifted.

The quenching action of added triethylamine can be seen in Fig. 5. Particularly small concentrations are sufficient for efficient quenching. The shape of
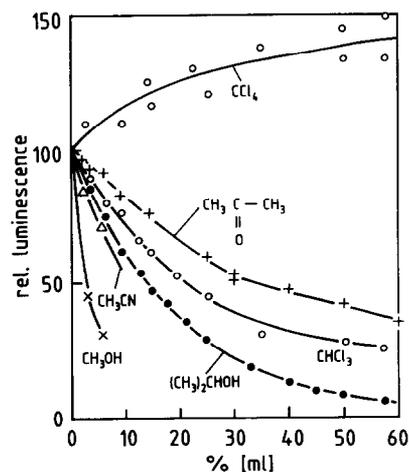

Fig. 4. Intensity of the luminescence of Si particles in purified cyclohexane suspension as a function of the volume fraction of added solvents. The suspension was aged in air for two days before the quenching experiments were carried out.
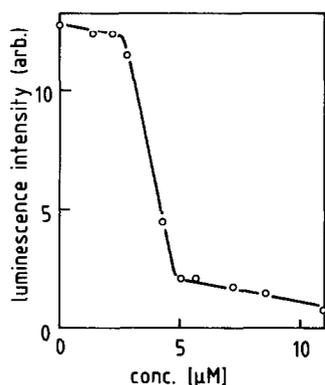
Fig. 5. Luminescence intensity of Si particles in cyclohexane suspension as a function of the concentration of added triethylamine.

the intensity versus concentration curve in Fig. 5 makes one conclude that quenching occurs in steps: in the beginning, little decrease in intensity is observed; a steep decrease then occurs followed by a much slower decrease at higher concentrations. Added ammonia had a similar effect as triethylamine.

The particles in solution are electrostatically charged. A suspension in cyclohexane, from which impurities were removed by the above procedure, was exposed to an electric field between two glassy carbon electrodes (2 mm diameter, 5 mm distance, potential: 40 V). After one hour, the anode had developed an intense luminescence, which shows that the particles in the cyclohexane phase are negatively charged. The experiment was also carried out with a cyclohexane suspension to which sulfuric acid (70%) had been added. It was found that H_2SO_4 quenches the orange luminescence to a large extent and that the particles migrate to the cathode to form there a red/orange luminescing layer. Obviously, the treatment with H_2SO_4 results in a change in the sign of the surface charge of the particles.
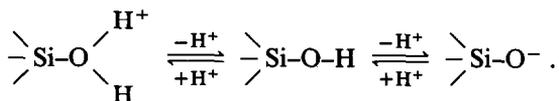
3. Discussion

The activation of the luminescence of the silicon particles in solution requires two components: hydrogen fluoride and oxygen. That oxygen is needed appears surprising at first sight as the particles already carry an oxide layer when formed in the combustion of silane. This oxide layer does not promote luminescence.

The fact that the red/orange luminescence develops in the non-polar cyclohexane phase in Fig. 1 is interpreted as only particles which are little oxidized on the surface being able to luminesce. Such particles have few polar groups on the surface and are therefore accumulated in the non-polar phase. The oxide layer of the particles in the lower polar phase is steadily attacked by hydrogen fluoride. The silicon particles with a non-polar surface then migrate to the non-polar upper phase where an equilibrium is established between surface oxidation and reduction by O_2 and HF, respectively, both reagents being present in the non-polar phase in low concentrations. According to this mechanism, more and more silicon particles are activated which explains the increase in luminescence intensity (in going from (B) to (C) in Fig. 1) but at the same time the silicon is consumed (to form SiF_4 via the reaction of HF with oxidized Si) which explains why the luminescence and absorption of the upper phase decrease at longer times. One would also expect that the silicon particles become gradually smaller with time which is possibly the reason for the blue-shift of the luminescence maximum (Fig. 3) and for the change in their UV absorption (Fig. 2, 60 h).

The quenching of the luminescence of semiconductor particles in solution has been studied for II–VI materials such as CdS [7]. Quenching occurs when adsorbed substances react with one of the charge carriers that are generated by light absorption in the semiconductor particle. One can then correlate the quenching efficiency to the relative positions of the electronic energy levels in the semiconductor and to the redox properties of the quenching substances. The curves in Fig. 4 cannot be interpreted straightforwardly in terms of the redox properties of the quenching solvents. The solvents that quench have no noteworthy electron affinity. For this reason, electron transfer from the illuminated particles to adsorbed quencher molecules is excluded. One could think that the quencher molecules interact with positive holes generated by light absorption. In fact, triethylamine, alcohol and ether are readily oxidized; however, other quenching solvents such as chloroform and sulfuric acid are hardly oxidized. One, therefore, also excludes positive hole scavenging by the quenching molecules.

Triethylamine and ammonia, the most efficient

quenchers, have base properties, and for this reason, one may suppose that their action consists of removing protons from the luminescence centers. On the other hand, sulfuric acid also quenches. As its interaction with the particles leads to a positive charge of the particle surface, one could believe that this interaction consists of a protonation reaction. Tentatively, we propose protolytic equilibria between the three surface structures:

$$\underset{/}{\overset{\backslash}{-}}Si-O\overset{\overset{H^+}{\diagup}}{\underset{\diagdown}{}}H \quad \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \quad \underset{/}{\overset{\backslash}{-}}Si-O-H \quad \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \quad \underset{/}{\overset{\backslash}{-}}Si-O^- .$$

(The nature of the remaining bonds of the Si atom are not known.) The neutral structure would be the center for the red/orange luminescence, wheres the charged structures would not be centers for luminescence. In the cyclohexane suspension, most of the surface structures are in the neutral state with a small contribution from the anionic one. Addition of polar solvents or bases shifts the equilibrium to the anion side. Addition of acid causes a shift to the cation side. The stepwise quenching of the luminescence in Fig. 5 could be explained by the existence of several centers on a particle, the deactivation of a few centers in the beginning not causing much luminescence decrease but causing a strong decrease when more centers already have been deactivated. It should also be noted that particles which carry Si–OH surface groups may stick together via hydrogen bonds; this aggregation could be governed by the protonation state of the surface. The influence of particle aggregation to the luminescence will be dealt with in a forthcoming paper. It may finally be mentioned that quenching of the luminescence by solvents [8] and by acids and bases [9] has also been observed for porous silicon.

Acknowledgement

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