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Physical degradation of a-Si films on thermal treatment: a scanning electron microscope study

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An *in situ* scanning electron microscope study of the effect of heat treatment on the structural integrity of undoped and phosphorus-doped glow discharge amorphous silicon films, deposited on crystalline silicon and pyrex 7059 glass substrates, has been undertaken. A similar, albeit more limited, investigation has been carried out on freely supported glow discharge films and one reactively sputtered Si-supported film. Glow discharge films, prepared at temperatures $> 70°$ C on silicon substrates, exhibit "blistering" of the surface at dehydrogenation temperatures, namely, $> 270°$ C. Ultimately, the "blisters" burst forming circular craters which reveal the underlying substrate. A similar phenomenon was observed in the case of a reactively sputtered film. In contrast, films prepared on silicon substrates at nominally room temperature exhibit more complex behaviour in which complete disintegration of the film occurs. Neither of the above effects was observed, on heat treatment, for amorphous silicon films which were either freely supported or deposited on pyrex glass.

1. Introduction

The burgeoning interest [1] in hydrogenated amorphous silicon (a-Si) results from the potential economic importance in the construction of photovoltaic cells and other semiconductor devices [2]. This material may be prepared by either of the complementary techniques of glow-discharge in SiH_4 or reactive sputtering. Thermal dehydrogenation of a-Si films commences at temperatures around 300° C with the evolution of hydrogen [3] and concomitant structural damage [4]. Whilst the mechanism of dehydrogenation has received considerable attention [3], little is known about the nature of the physical degradation of the film and the manner in which the electrical and optical properties are subsequently influenced.

In this paper we report on an *in situ* scanning electron microscope study (SEM) of damage induced in a-Si films, both supported and freely supported, by heat treatment.

2. Experimental details

Thin films ($< 1\,\mu m$) of a-Si, both undoped and phosphorus-doped, were prepared by glow discharge in SiH_4 and $SiH_4/PH_3/Ar$ mixtures, respectively, on crystalline silicon, pyrex Corning 7059 glass or NaCl substrates as previously described [5, 6]. The films prepared on single crystal NaCl were used to prepare freely supported films by a flotation technique [6]. One reactively sputtered film was also investigated. The conditions of film preparation are summarized in Table I.

Changes in the film surface, on heating the material to 350° C, were monitored by a scanning electron microscope (Cambridge Stereoscan). The films were mounted on an electrically heated copper stage within the electron microscope. The film temperature was measured with a chromel–alumel thermocouple, embedded in the copper block, with the thermocouple tip situated 5 mm from the film. The heated stage was constructed to

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TABLE I Preparation conditions of glow discharge a-Si films*

Number	Substrate	Deposition temperature (°C)	Pressure of SiH_4 (Torr)
(i) Undoped			
227	Si	103	0.16
239	Si	70	0.16
254	Si	24–27.5	0.15
259	Si	98 – 105	0.15
129	glass	200	0.11
259	glass	98–105	0.15
261	NaCl	100	0.16
262	NaCl	95–104	0.15
(ii) Phosphorus-doped			
193	Si	218	0.11
203	Si	220	0.11
258	Si	231–223	0.19
258	glass	231–223	0.19
260	NaCl	102–107	0.19

*r.f. power = 20 W (film 129 = 10 W). Sputtered film prepared with 1.5 m Torr H_2/3.7 m Torr Ar mixture at 110°C.

give good thermal contact between the film substrate and the copper block. The specimens were heated at a rate of 3 to 5°C min^{-1} until a maximum temperature of 350°C was attained; micrographs were continuously obtained throughout the temperature range. X-ray dispersive analysis of the doped films showed the presence of Si, P and, in the case of self-supported films only, Cl derived presumably from the flotation technique. Argon was not detected in the doped a-Si films.

3. Results

The films listed in Table I were studied. They may be categorized as (i) undoped and phosphorus-doped films prepared at temperatures between 70 and 200°C (hereafter referred to as high-temperature films (ii) undoped films prepared nominally at room temperature (low-temperature films) and (iii) one undoped reactively sputtered film.

3.1. High temperature films

3.1.1. Silicon substrate

Fig. 1a shows a micrograph of an as-prepared film (239) prior to heat treatment. The surfaces of all the films investigated, typified by Fig. 1a, were smooth and featureless at a magnification of up to ×1200. Each film was subsequently heated and, typically, "blisters" with a circular cross-section were first manifest on the surface at 275 ± 10°C as shown in Fig. 1b. The blister diameters, when initially observed, were 50 ± 15 μm with a number density of approximately 9 x $10^2 cm^{-2}$. Upon further heating the size and number density of the blisters increased (Fig. 1c). For example, at ~290°C there were typically 2 x 10^4 blisters cm^{-2} exhibiting a range of ~40 to ~130 μm; the distribution of blisters was independent of their position on the film.

At ~300°C a number of the blisters burst (Fig. 1d) with sufficient ferocity to reveal the underlying substrate and, on inspection of the micrographs, remnants of the "blister caps" were seen to rest on the vicinal surfaces. Exfoliation continued until virtually all the blisters had burst (Fig. 1e). Ultimately, at the maximum attainable temperature of 350°C, the remaining blisters had burst to produce a cratered surface (Fig. 1f) in which 40 to 60% of the sufrace film area remained intact. The behaviour was common to both undoped and phosphorus-doped films.

3.1.2. Glass substrates

No blistering, cracking or other physical defect of a-Si films on glass substrates was observed under the conditions described previously.

3.1.3. Freely supported films

Two freely supported a-Si films were studied but such films were physically unaffected by heat treatment. Occasionally, freely supported films cracked across the entire film.

3.2. Low-temperature films

The behaviour of these films, under similar conditions, were very different from the equivalent high-temperature films. At 350°C almost total disintegration of the film was evident to produce the characteristic striated structure shown in Fig. 2. Onset of microscopic film cracking occurred at 348°C.

3.3. Sputtered films

A reactively sputtered film, supported on a silicon substrate, was studied for comparison with glow discharge films. The characteristics of the film degradation were identical to silicon-supported high-temperature glow discharge films (Fig. 1a to e) in that blistering and subsequent bursting and cratering occurred on heating. However, the onset of the blistering process was evident, in this film at least, at a lower temperature of ~230°C.

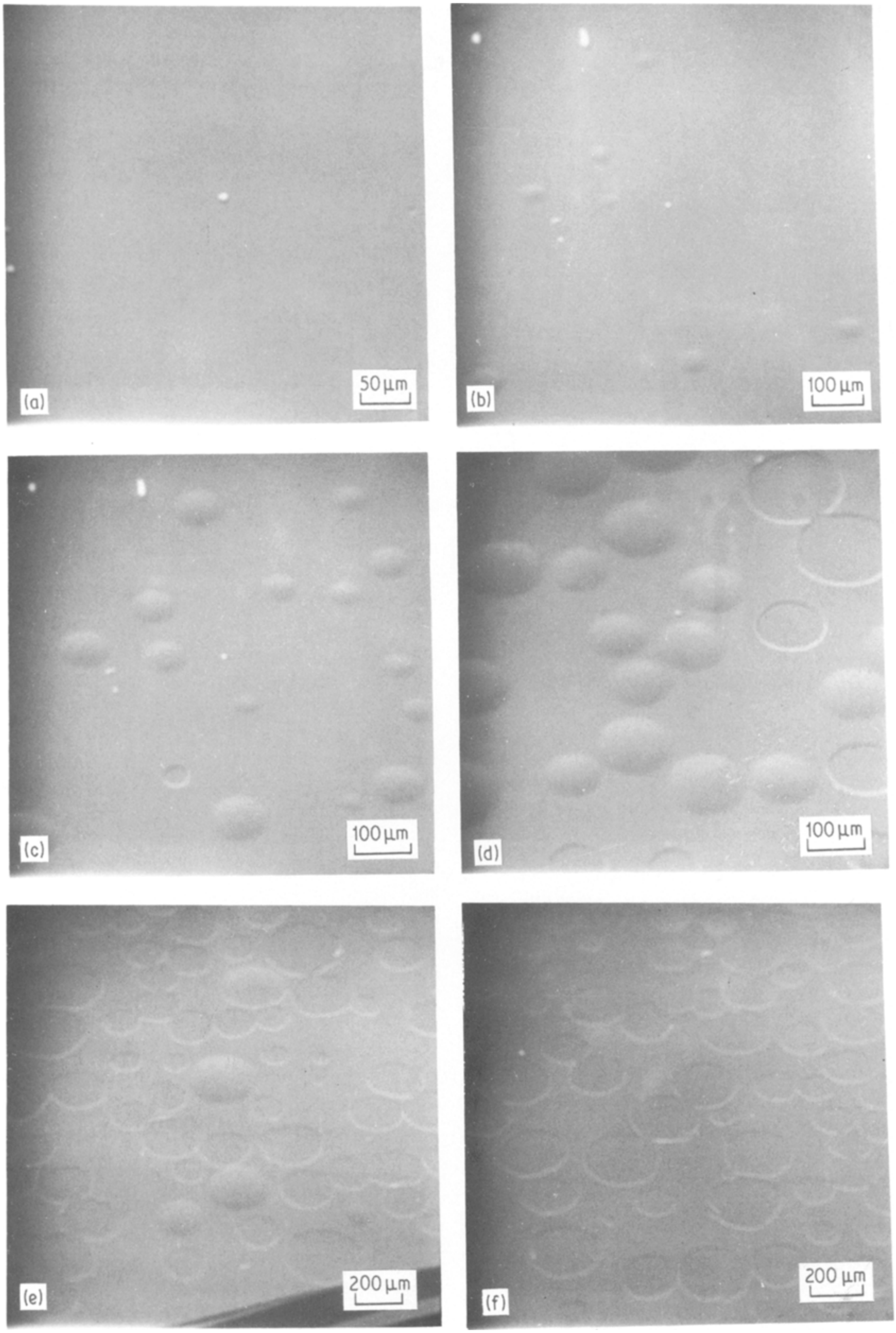

Figure 1 Scanning electron micrographs of an a-Si film (239; Si(c) substrate; deposition temperature 70° C) at (a) room temperature and on heating to (b) 273° C, (c) 290° C, (d) 303° C, (e) 335° C, (f) 350° C.

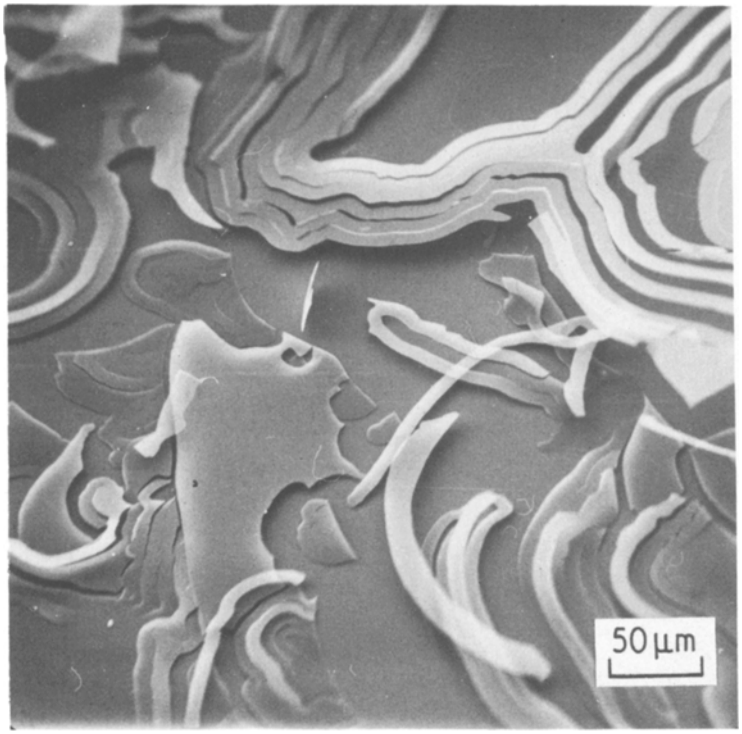

Figure 2 Striated fractures caused by heat treatment of an a-Si film (254; Si(c) substrate; deposition temperature 25° C) on heating to 348° C.

4. Discussion

On heating a-Si films, up to 350° C, three distinct types of degradation process have been observed by electron microscopy.

(i) Local detachment of the film from the underlying substrate causing blistering of the films followed by exfoliation and subsequent cratering. This behaviour is associated with high-temperature films and one hydrogenated sputtered film; both types were deposited on and supported by crystalline silicon.

(ii) Gross disintegration of the film structure associated with low-temperature films on a silicon substrate.

(iii) Films which were apparently unchanged. This behaviour was characteristic of both high-temperature films on glass substrates and self-supported films.

The characteristic blistering phenomena, e.g. Fig. 1a to e, can be explained by the evolution of gas within the film accentuated by thermal heating. This gas may, conceivably, be either occluded after incorporation during the film preparation or hydrogen produced by thermal dehydrogenation [3]. In the case of doped films the occluded gas may be PH_3 or Ar in addition to H_2 and SiH_4 which could be conceivably trapped within the amorphous framework in both types of film. Both mass spectrographic analysis [8] of the evolved gas and electron microprobe determinations of the elemental composition of the films prior to heating eliminates Ar as an occluded gas in the doped films. Infra-red spectra of the doped films do not exhibit phosphorus–hydrogen stretching bands due to occluded PH_3; in both types of films silicon–hydrogen stretching modes due to SiH_4 are absent. The features of the blistering phenomena are common to both doped and undoped films and suggests that the evolved gas emanates from a common source in both types of film. Analysis of similar freely supported undoped a-Si films by 25 MeV α-particle scattering [6] demonstrates that the films contain only silicon and hydrogen plus traces ($<$ 1 at%) of oxygen. Therefore we propose that the evolved gas is hydrogen which arises from the thermal dehydrogenation [3] of the films. We cannot exclude, at this stage, a relatively minor loss of occluded H_2 at low temperatures since thermal hydrogen evolution does not occur [3] at a measurable rate at temperatures less than ~300° C. Manometric measurements of the pressure changes during the thermal treatment of supported a-Si films and the crystalline silicon substrate demonstrated that the substrate does not evolve gas. The infra-red spectra of the silicon substrate do not exhibit bands attributable to silicon–

hydrogen bonds. Hydrogen evolution observable on heating the supported a-Si films is consequently associated with the hydrogenated amorphous material rather than the crystalline substrate.

In view of the absence of blistering of self-supported films it seems reasonable to suppose that a fraction of the gas may diffuse towards the film-substrate interface and is trapped in microscopic voids. Such voids may be inherent defects arising from the original deposition procedures. The pressure increase in these voids causes the blisters to expand until, ultimately, the blisters burst once the fracture stress caused by the internal gas pressure of the film is exceeded. In this context we have observed (unpublished data) sudden increases in gas pressure during manometric studies of the thermal dehydrogenation of supported a-Si films maintained in vacuo. Previous studies [7] of ion-implanted metals, for example, hydrogen-implanted Fe, have shown that gas evolution causes similar surface blistering.

The reason for the resistance of high-temperature films supported on glass substrates to blistering is not immediately clear. It is relevant to note, however, that Jones *et al.* [8] have recently reported that only 50% of the hydrogen evolved from a-Si films on 7059 glass substrates can be detected by manometric measurements. They conclude that 50% of the hydrogen must have diffused into, and be retained within, the glass substrate. In contrast, the hydrogen devolution from a-Si films on aluminium [8] and crystalline silicon [9] is reported to be quantitative.

The diffusion coefficient of H_2, at 400° C, in crystalline silicon is $2.6 \times 10^{-6} cm^2 sec^{-1}$[10]; a value which is an order of magnitude greater than that in silica [10] or Vycor glass [11] at the same temperature. It is a reasonable assumption that the diffusion coefficient of H_2 in crystalline silicon represents a lower bound to that in the amorphous material. In the case of silicon-supported films, there exists a diffusion barrier due to the oxidized layer present on the silicon substrate. It has been suggested previously [11] that permeation of gases through Vycor glasses occurs through microscopic diffusion channels. Interfacial diffusion or molecular streaming through such channels may preclude the accumulation of gas at the interface and the blistering phenomena would be suppressed.

The striated fractures and disintegration of low-temperature films can also be associated with gas evolution although thermal stress effects may be involved. Moreover, the morphology and distribution of silicon-bound hydrogen of high- and low-temperature a-Si are known to differ [6, 12].

5. Conclusions

It has been demonstrated that the physical degradation of a-Si films during heat treatment is both film and substrate dependent. Heat treatment of such films can lead to gross physical damage especially for films prepared on silicon substrates. It is clear, therefore, that it can not be tacitly assumed that the integrity of these films is preserved at high-temperature measurements which are likely to be affected by these phenomena.

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