INVESTIGATION OF DEFECTS IN AMORPHOUS SILICON FILMS USING POSITRON ANNIHILATION

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Positron lifetime studies have been carried out on amorphous silicon films prepared by sputtering. Isochronal annealing at different temperatures has been investigated for understanding the microstructure such as vacancies and microvoids. The shortest lifetime component is attributed to the annihilation with the bulk electrons in the crystalline substrate. Information concerning the effective volume of the dominant vacancy type defect, quadrivacancy, in the films is obtained from the study of the middle lifetime component. The appearance of the longest lifetime component ($t \approx 2$ ns) suggests the existence of large microvoids in the films.

Although the technical use of amorphous semiconductors (notably Si) has prompted considerable interest in recent years, the investigation of amorphous silicon has mainly been done by electrical conductivity measurements, optical absorption, electron spin resonance, and also by electron microscopy [1], etc. However, none of these methods leads in itself to a determination of very small vacancy-type defects! Positron annihilation depends upon the electron density at the site of the positron and can be used to characterize the nature of the positron-trapping site. This technique has been successfully used to study the defects in materials. In the present paper, we report the results of positron annihilation studies on relatively thick (≈ 10 μm) amorphous silicon (a-Si) films. Through this study it is possible to infer the existence of clusters of vacancies and microvoids in a-Si. The variation of annihilation parameters with the annealing temperature of the films is explained satisfactorily. Even though some positron annihilation experiments on a-Si have been

published [2–9], to our knowledge there is still no definite conclusion.

All a-Si samples were rf-sputtered onto polished p-type single crystal silicon wafers. The film thickness is about 10 μm which was achieved by sputtering an n-type (10 Ω cm) single crystal silicon wafer in an argon atmosphere. The deposition conditions were as follows: Prior to sputtering pressure, 1×10^{-6} Torr; during sputtering pressure, 1×10^{-2} Torr; substrate temperature, 300 K (the substrate holder is water cooled); and RF power, 60 W. The infrared absorption spectrum of a-Si as measured by a Perkin-Elmer (model 710 B) double-beam spectrometer shows no detectable Si–H stretching mode occurring at 2100 cm^{-1} . Thus, we presume that the effect of hydrogen on the positron annihilation measurements can be ignored.

The positron source was a 1 μCi Na^{22}Cl source deposited on a mica foil. The counting rate was 40 counts per second and each spectrum contained 2×10^6 counts. The full width at half maximum

(FWHM) of the resolution function was about 450 ps. Analysis of the lifetime spectra was done using the POSITRONFIT extended program [10]. The resolution function was approximated by one gaussian. There was no source correction which was expected to be of little importance in this experiment. All positron measurements were carried out at room temperature. The isochronal annealing was performed in an infrared radiation furnace. Each isochronal annealing step lasted for 30 min. During the annealing and natural cooling processes, samples were placed in a quartz tube with a flow of dry nitrogen.

The lifetime spectra were fitted by three components with intensities and lifetimes designated as (I_1, t_1) , (I_2, t_2) , and (I_3, t_3) , respectively. The shortest lifetime has a value of 208 ± 10 ps which does not change with increasing the annealing temperature up to 700°C as shown in fig. 1. This lifetime was not fixed during the analyses, thus serving as a check on the individual measurement, and proved independent of annealing temperature. t_1 has been attributed

Fig. 1. Lifetime t_1 and the corresponding intensity versus isochronal annealing temperature. The lines drawn through the data are used to guide the eye only.

to the positrons trapped in shallow traps in a-Si by He et al. [2] and Bhidé et al. [3]. We believe that this lifetime should correspond to the annihilation of positrons with the bulk electrons in the crystalline silicon, where positrons have penetrated through the amorphous film and into the crystalline silicon. Since Dannefaer et al. [4] have performed a positron experiment on a-Si having a thickness of only $1\ \mu\text{m}$, no response except for the t_1 bulk lifetime could be detected. Thus, t_1 cannot be due to the annihilation of positrons in an amorphous film or on the surface between the a-Si and the c-Si, otherwise t_2 should also be observed in the experiment of Dannefaer et al. [4]. The decrease in I_1 at 450°C as shown in fig. 1 is the result of the increase of positrons trapped in the a-Si defects which will be discussed below.

The relation between the middle component t_2 and annealing temperature is shown in fig. 2. This lifetime has a constant value of 420 ± 20 ps below about 450°C , after which temperature it starts to decrease. The corresponding intensity I_2 component is also shown in fig. 2. It keeps constant below 450°C , while above that temperature I_2 increases sharply. In an earlier paper [11] the lifetime in divacancies and

Fig. 2. Lifetime t_2 and the corresponding intensity versus isochronal annealing temperature.

quadrivacancies was determined to be 325 ± 20 and 435 ± 30 ps, respectively, while for monovacancies, Fuhs et al. [12] determined a lifetime of 266 ± 10 ps. Comparing these results, we can therefore say that the effective volume of the most dominant vacancy type defect in a-Si is quadrivacancy when the annealing temperature is below 450°C . There are two important factors which will influence the t_2 component at higher annealing temperature. First, Fang et al. [13] have performed the gas emission experiments which show that argon escapes around 400°C . If the argon is released, the number of vacancies will increase and hence the increase in I_2 at 450°C could be a result of the release of argon from the silicon film. Thus, the decrease of the annihilation intensity I_1 of positrons with the bulk electrons in the crystalline silicon at 450°C as shown in fig. 1 is the result of the increase of positrons trapped in the a-Si vacancies which reduces the number of positrons penetrating into the c-Si. The continuous decrease in t_2 after 450°C can be explained by the fact that after argon escaping the annealing causes the mean defect volume to reduce such that the mean result of the t_2 component decreases. Second, the a-Si films are known to crystallize in the temperature range 600 – 700°C . It is thus reasonable for larger vacancies to break down to become smaller vacancies at crystallization. Thus, the crystallization will also increase the intensity I_2 and decrease the lifetime t_2 .

The longest lifetime t_3 and the corresponding intensity I_3 are shown in fig. 3. It can be seen that t_3 keeps constant and has a value of 2 ns below 400°C , increases with temperature up to 3 ns at 650°C , and then sharply drops down. I_3 decreases below 400°C , increases with temperature until 650°C , and then sharply drops down. This component can possibly arise from the positronium formation in the microvoid. He et al. [2] and Bhide et al. [3] have carried out angular correlation experiments of positron annihilation radiation (ACPAR) in a-Si, and confirmed the formation of positronium which they supposed is formed in microvoids. Their origin has been attributed to a lack of surface mobility of the deposited atoms and to a mechanism which relieves the strain in the amorphous network [14]. The decrease in I_3 below 400°C may be due to the rearrangement of the amorphous network which will decrease the number of microvoids. When the annealing

Fig. 3. Lifetime t_3 and the corresponding intensity versus isochronal annealing temperature.

temperature is above 400°C , the trapping centers (divacancies and quadrivacancies) aggregate to form microvoids or migrate to connect with the microvoid and increase the size of the microvoid. Thus, I_3 and t_3 both increase. When the films start to crystallize at 650°C , the microvoids break down and I_3 and t_3 decrease sharply.

Positron annihilation studies in a-Si films formed by sputtering have shown that the effective volume of the most dominant vacancy type defect is quadrivacancy when the annealing temperature is below 450°C , and that there exist microvoids. The variation of the intensity and lifetime of the three components in the lifetime spectra I_1 and t_1 ($t_1 \approx 210$ ps due to annihilation with bulk electrons in the crystalline substrate), I_2 and t_2 ($t_2 \approx 420$ ps due to trapping in quadrivacancies), and I_3 and t_3 ($t_3 \approx 2$ ns due to formation of positronium in microvoids) with the isochronal annealing temperature has helped in understanding the a-Si microstructure. The positron annihilation technique has thus proved a useful tool to characterize amorphous semiconductors.

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