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Roles of SiH_4 and SiF_4 in growth and structural changes of poly-Si films

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Abstract

The structural properties of polycrystalline silicon films, prepared by plasma enhanced chemical vapor deposition system, with different flow rates of SiH_4/SiF_4 mixtures at 300 °C were investigated. This study indicates that the low hydrogen coverage on the growing surface, under optimum fluorine radicals, will be leaded to an improvement of crystallized area as compared with case of high hydrogen coverage surface. Moreover, the studies of the role of SiH_4 and SiF_4 radicals show that the SiH_4 radicals are important in the nucleation and growth of grains. However, SiF_4 radicals are effective in the structural change of grain boundaries regions and by this way, in the present system, establish the growth of grains under the dominant $\langle 1\,1\,0\rangle$ direction. The stress investigation indicates that addition of high flow rate of SiF_4 in amorphous film, results in the nearly stress free films. Finally, we found that the changes in *g*-value reflect the changes in the intrinsic compressive and tensile stress in the both polycrystalline and amorphous silicon films.

Keywords: Plasma-enhanced chemical vapor deposition; Polycrystalline thin films; Preferential orientation; Low-angle/high-angle grain boundary; Hydrogen coverage; Crystallization; *g*-Value of electron spin resonance; Stress

1. Introduction

Polycrystalline silicon films (poly-Si) have attracted intensive interest because of the potential to prepare high performance and large area semiconductor devices such as solar cells [1,2] and thin film transistor (TFT) in flat panel displays [3–5]. The direct deposition of poly-Si films at a temperature below the strain point on the glass substrates is an attractive and economical technology for producing silicon displays. For this purpose, recent main research subjects are low-temperature deposition of poly-Si films, which can be widely used in the active-matrix liquid–crystal displays that are now typically found in computer technologies and an increasing number of monitors.

In the poly-Si films, the charge carrier mobility as an important parameter in the electrical properties is mainly determined by polycrystalline structure. Polycrystalline silicon materials are typically heterogeneous and anisotropic consisting of crystalline grains and amorphous-like silicon tissue in grain boundaries (GBs). The GBs and intregranular defects can act as electrical potential barriers and scattering sites, which decrease the carrier transport mobility and also serve as midgap states working to increase the leakage currents [6]. A reduction in the GBs effects is a key to enhance the TFTs performance. Some methods for this purpose are as follows. The low oxygen content that avoids extrinsic GB activation [7,8] and high hydrogen incorporation that results in passivation of the Si dangling bonds in the GBs, which decreases the density of GBs states in the film [9,10]. The reduction in the GBs regions by an increase in the grain size is another method to reduce the GBs effects and laser crystallization is a well-known method for this purpose [11]. However, high cost and poor film uniformity reduce some of the advantages of this technique. Beside the above-mentioned methods that cause a reduction in the effects of GBs, the formation of low-angle GBs that is responsible for a preferential oriented

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structure, also may enhance the transistor characteristics [12]. The low-angle GBs are those GBs that the angle between the two grains is small (<10°). The low-angle boundaries can be represented as an array of dislocations that the regions of the two grains placing in between the dislocations are in good match with each other. In such GBs, cores of dislocation are regions of poor fit with highly distorted crystal. However, when the angle between two grains is above 10–15°, a high-angle boundary is formed and has amorphous-like structure. In high-angle boundaries, the dislocation spacing is so small that cores of individual dislocations start overlapping; therefore, individual dislocations can no longer be physically identified. The differences between low-angle and high-angle GBs can be summarized as follows:

- High-angle boundaries contain large areas of poor fit while low-angle boundaries contain large areas of good fit separated by misfit dislocations.
- High-angle boundaries have an open structure with lots of free volume while low-angle boundaries have little free volume.
- In case of high-angle boundaries, the interatomic bonds are either broken or highly distorted at the boundary while in case of low-angle boundaries the interatomic bonds are only slightly distorted.

Moreover, in the previous article [13], we reported that the high degree preferentially oriented poly-Si films, prevents the oxygen contamination owing to establishment of the low-angle GBs regions in such films. These properties for the low-angle GBs indicate that the growth of poly-Si films with a preferentially orientation seems to be a key to enhance the TFTs performance by reducing of defects and oxidation rate in the GBs regions. In that work [13], the poly-Si films with $\langle 1\,1\,0\rangle$ texture were deposited by plasma enhanced chemical vapor deposition (PECVD) method using a SiH_4/SiF_4 system. In the present work, in order to enhance the degree of the $\langle 1\,1\,0\rangle$ preferential orientation and to reduce the defects, such as stress in these films, we investigate mechanism of addition of SiH_4 and SiF_4 on the enhancement of crystallization and preferentially orientation of poly-Si films by using different flow rate of SiH_4, [SiH_4], and flow rate of SiF_4, [SiF_4].

2. Experimental details

Polycrystalline Si films were deposited by PECVD system at a temperature of 300 °C using SiH_4/SiF_4 mixtures in a hot wall type fused quartz reactor, employing the inductive coupling of rf power at 13.56 MHz. This deposition system has been presented elsewhere [14]. In this work, a diluted gas of SiF_4 with He gas (SiF_4: 5%, He: 95%) was used. Therefore, the net flow rate of SiF_4 was changed between 0 and 0.5 sccm under five different conditions of $[SiH_4] = 0.2$, 0.5, 1, 2, and 5 sccm. The film thickness was kept at 0.5–0.6 μm by varying the deposition time. The rf power and gas pressure during film deposition were maintained at 20 W and 33.3 Pa, respectively. The unique feature in the preparation process of the samples before deposition of the poly-Si films is that the substrate were sequentially exposed to the hydrogen and nitrogen plasma for 20 min to make their surface clean. The plasma exposure also causes the change in the surface roughness [15], beside the above-mentioned surface cleaning effects. In a previous paper [15], we have reported that the presence of a proper degree of the surface roughness improves the crystallinity and increases the grain size [15].

Polycrystalline Si films were deposited on glass (corning 7059) substrate for measurements of X-ray diffraction (XRD), Raman scattering and stress. The single $\langle 1\,1\,1\rangle$ crystal Si substrate with a resistivity higher than $10^3\ \Omega$ cm was used for infrared (IR) absorption measurement and electron spin resonance (ESR). For the ESR measurement the fused quartz substrate was also used to investigate effects for the use of the different substrates in addition to the above crystal Si substrates with a proper oxidized layer. As a result, we did not find significant difference between the ESR spectra for the samples on both substrates. The morphology was investigated by XRD measurement. The degree of preferential orientation in $\langle hkl\rangle$ texture was represented by X-ray relative intensity, $I_{\mathrm{XRD}}(\langle hkl\rangle)$, for a given texture, which was normalized by the corresponding X-ray intensity for Si powder with a roughly completely random texture. The different film thickness in each sample was also corrected using the absorption coefficient of X-ray for Si. The details for the results of the I_{XRD} were presented in a previous paper [13]. The grain size, δ, in a given depth direction was estimated from the half-width value of the corresponding X-ray spectra by means of the Scherrer formula.

The crystallization ratio (volume fraction of crystalline phase), ρ, was estimated from the intensity of the Raman spectra using the procedure proposed by Tsu et al. [16]. The Raman spectra was decomposed into two components with narrow and broad line shapes corresponding to a crystalline Si phase (c-phase) at around 520 cm^{-1} and an amorphous Si phase (a-phase) at around 480 cm^{-1}. The third component between 480 and 520 cm^{-1}, due to very small crystallites, was relatively weak; therefore, we ignored the contribution of it to the values of ρ. Then the ρ values were estimated from the intensity ratio of both the a- and c-phase components [16]. Therefore, the real ρ values may be somewhat different from the values shown in the diagram. The g factor was measured using an X-band ESR spectrometer with magnetic-field modulation frequency of 100 kHz, and the measurements were carried out at room temperature. The infrared vibrational absorptions were measured using a Fourier-transform spectroscope at a normal light incidence.

The film stress was estimated from changes in the curvature of the substrate/film system with a rectangular shape (the length L being sufficiently longer than the width), using Stoney's formula [17] as: