In this work a study of Low Pressure Chemical Vapour Deposition (LPCVD) of Germanium-Silicon films has been carried out. The films were deposited on thermally oxidised silicon wafers using a horizontal hot-wall LPCVD system, at deposition temperatures ranging from 430 to 480 °C and total pressures from 3 to 200 Pa. Pure GeH₄ and SiH₄ gas sources were used for the experiments. Growth kinetics and texture of GeₓSi₁₋ₓ films versus varying deposition conditions, resulting in different film properties, were investigated. The effect of Germanium content in the layers on deposition rate at 430 °C and the change in the film crystallinity caused by deposition at different deposition pressures were studied.

INTRODUCTION

Polycrystalline GeₓSi₁₋ₓ has received attention [1-7] because of the possibility of band-gap engineering by varying the Germanium content. It became attractive as a new material for deep sub-micron CMOS gate electrodes due to its better work function of p-type doped GeₓSi₁₋ₓ compared to poly-Si [8]. It has also been demonstrated to be a material with high compatibility to CMOS processing.

Polycrystalline GeₓSi₁₋ₓ can be grown from a mixture of SiH₄ and GeH₄ as reactive gases in a conventional LPCVD system. Several major problems make the growth of polycrystalline GeₓSi₁₋ₓ more difficult with respect to poly-Si growth. Firstly, the initial formation of the GeₓSi₁₋ₓ nuclei on the SiO₂ surface is retarded. The incubation time, depending on deposition conditions, varies from a few seconds up to tens of minutes. The second important problem is relevant to the texture of the films. To obtain a uniform dopant distribution, a fast diffusion along the grain boundaries is necessary. For this purpose, a (110) orientation of the grains resulting in its near-cylindrical columnar structure is desired. Thirdly, a higher reactivity of GeH₄ compared to SiH₄ leads to a depletion of the gas mixture from GeH₄ in the downstream direction of the reactor. This gradual change in the gas composition causes differences in deposition rate and germanium content measured for the films placed in a long waferboat. The film properties (texture, morphology) depend strongly on the composition and, therefore, are influenced by the germane depletion.

In this work, a study of LPCVD of GeₓSi₁₋ₓ films has been carried out. Growth kinetics, composition and texture of the GeₓSi₁₋ₓ (X=0.3-0.65) films were studied versus deposition parameters. Optimum deposition conditions resulting in high-quality GeₓSi₁₋ₓ layers are proposed.
A 25-nm thick SiO$_2$ layer was grown by means of thermal oxidation at 950 °C in a dry-O$_2$ ambient on 3-inch (100)-oriented n-type Si wafers with a resistivity of 2-5 Ohm-cm. To prevent a surface inferiority, the deposition experiments were started within 30 minutes after the oxide growth. To avoid the incubation time, a few-nm thick amorphous silicon layer was pre-deposited using the same LPCVD system. Deposition of the Ge$_x$Si$_{1-x}$ films was immediately started, without vacuum break.

A hot-wall horizontal LPCVD system has been used for the experiments. A furnace of 1-m total length contained three independent resistive heaters to ensure a close-to-flat ($\pm 2$ °C) temperature distribution in the 30-cm central part of the furnace, where the waferboat was situated. Both high-purity SiH$_4$ and GeH$_4$ were mixed in the gas line before introduction into the reaction tube.

The film thickness measurements were carried out by means of a DEKTAK 3030 profile-meter on an etched step. The Germanium fraction in the layers was measured using an Energy Dispersive X-ray Analyser (EDX), calibrated with standard pure-silicon and pure-germanium samples. The layer texture was obtained with a Philips x-ray Diffractometer (XRD), irradiating the CuK$_{\alpha}$ line of 1.5406 Å. Based on the (220)-XRD peak position, it was possible to measure the Germanium content in a thin (down to 50 nm) Ge$_x$Si$_{1-x}$ layer.

**EXPERIMENTAL RESULTS AND DISCUSSIONS**

**Deposition Kinetics Influenced by Film Composition**

For pure silicon, grown from SiH$_4$ at low deposition temperature of 430 °C, the deposition rate is in order of a few nanometer per minute. In this regime, the surface is fully covered with hydrogen and its desorption is mostly the rate limiting step [9]. Admission of GeH$_4$ enhances the hydrogen desorption due to a catalytic action of adsorbed Germanium [10, 11]. As a consequence, deposition of pure germanium at the lowest temperature of 430 °C occurs without limitations given by the hydrogen desorption, because the surface is free of hydrogen [9]. Although the deposition kinetics of poly-Ge$_x$Si$_{1-x}$ (X=0.3-0.65) films is strongly governed by the film composition, we could not find publications studying this behaviour at such a low temperature.

At a fixed deposition temperature of 430 °C, the deposition rate gradually increases with increasing Germanium fraction ($At\%_{Ge}$) in the Ge$_x$Si$_{1-x}$ films up to 50 atomic percent (Fig. 1). The region between 50 and 60 atomic percent has a crucial influence on the deposition rate, which drastically increases. This can be explained in terms of the hydrogen desorption. To understand this better, let us consider the relative amounts of Si-Si, Ge-Si, and Ge-Ge bonds in the crystalline material with a diamond lattice. Apparently, desorption of hydrogen from a Ge-Ge site demands overcoming the lowest energy barrier with respect to desorption from a Ge-Si site or, especially, from a Si-Si site. The Si-Si bonds dominate for slightly Ge-doped silicon, whereas the relative amount
of the Ge-Ge bonds is negligible. An increase of the Ge content to 50 atomic percent leads to a change in the bond shares. Let us make the simplified assumption that the relative amount of the Ge-Ge bonds is a major factor determining the hydrogen-desorption rate and, therefore, the activation energy behaviour. Let us also assume that Ge$_{0.5}$Si$_{0.5}$ has a maximum density of the Ge-Si bonds. This is probably true, if a uniform distribution in the material bulk is taken into account. Furthermore, we assume an absence of both the Si-Si and Ge-Ge bonds in this material. This could be true in an ideal case of uniform distribution of Germanium atoms in the lattice. According to diamond lattice properties, each Si atom in the as-composed material is bound to four Ge atoms and vice versa. Therefore, a substitution of a silicon atom with a germanium atom will create four Ge-Ge bonds. This means that the hydrogen desorption will be dramatically enhanced with increasing the $\text{Ar}^{\%}\text{Ge}$ beyond 50 percent, due to the avalanche in formation of new Ge-Ge bonds.

As one can expect, the GeH$_4$ share in the gas phase crucially influences the Germanium content in the films (Fig. 2). This is in agreement with [12, 13]. Since the sticking probability for GeH$_4$ is more than 3 times higher with respect to that for SiH$_4$ [9, 14], germane adsorbs more intensive compared to silane. As can be noticed from Fig. 2, a 30%-volume share of germane gives 60 atomic percent of Germanium in the films. According to the model in [9] this corresponds to a sticking probability ratio between GeH$_4$ and SiH$_4$ of 3.9 in contrast to 3.2 mentioned in [9]. This difference is probably due to the lower deposition temperature we used. The high sticking probability ratio results in a relative GeH$_4$ depletion from the gas mixture, further resulting in changing the germane-to-silane partial pressure ratio along the precursor-drift direction.

To evaluate the GeH$_4$ depletion in the downstream direction, the gas consumption model has been developed, based on the experimental dependencies ($V_{\text{dep}}$ versus: $T_{\text{dep}}$, $P_{\text{tot}}$, Ge content, etc). The dependencies were obtained for the first measuring wafer in the waferboat. The temperature profile along the furnace length was also measured and taken into account. By applying a simplified model ignoring diffusion, it was possible to simulate the properties for more than 60 wafers situated in the waferboat. Ignoring the diffusion is based on our previous experiment [15] regarding plasma deposition at low pressure of 2 Pa. It has been shown by means of the optical measurements that at a total flow-rate of 100 sccm the upstream diffusion of SiH$_4$ was significantly suppressed. An increase of the pressure led to a less diffusion. For the present work, the higher pressure of 20 Pa had to cause even a weaker diffusion.

The model assumes that insignificant gas consumption takes place before the first measuring wafer. This is because of the furnace temperature increases rapidly near the flat zone and the gas diffusion is ignored. The model considers a separate gas volume moving step by step from the entrance of the reactor to the exit, without mixing with other volumes. During the first discrete step, deposition of a layer with composition determined by the input parameters (temperature, total pressure, GeH$_4$/SiH$_4$ ratio). After this step, the gas consumption is taken into account and a new-composed gas volume is calculated. Hydrogen, added to the volume due to the precursor decomposition, causes an increase of the volume size because of the total pressure constancy. The drift velocity of the volume will be proportionally increased. Figure 3 depicts computed germane share in the gas phase along the downstream direction, at different total pressures. Figure 4 compares simulated and experimental deposition-rate distributions along the waferboat.
Because of a good agreement, we can finally describe the deposition process in the following steps: a) the local germane-to-silane pressure ratio determines the film composition at the chosen reactor space; b) within this space, the film composition has a crucial impact on the deposition rate, especially for $A_{Ge}^{\%}$ between 50 and 60 percent; c) due to the precursor consumption, a new local germane-to-silane ratio is formed in the downstream direction.

**Film Texture versus Deposition Conditions**

There are several important parameters, which determine the orientation of Ge$_x$Si$_{1-x}$ crystallites to be grown [16]. Dependence on deposition temperature refers to surface mobility and hydrogen desorption. Gas-flow ratio governs the film composition, which certainly influences the texture from hydrogen desorption point of view. Deposition pressure affects the nucleation process because of the surface-collision frequency. High pressures cause formation of the amorphous material due to gas phase reactions.

As follows from Figure 5, the films typically contain both (110) and (111) oriented grains. In some spectra a weak (311) peak appears. It has been found that the (110)-to-(111) ratio strongly depends on the film thickness, for a wide pressure range. In fact, the growth of the (111) grains is completely stopped beyond a film thickness of about 100 nm (Fig. 5). On the one hand, the (111) grains can eventually be overgrown by the (110) grains due to a faster growth rate of the (110) planes compared to the (111) planes. On the other hand, a re-nucleation on the (111) surface can also be possible. Additionally, for the equivalently thick films, the total pressure influences the (110) grain share. An increase of the total pressure causes an increase of the (110) share for equivalently thick layers. This probably arises from nucleation matters.

The following experiments have been carried out to investigate the pressure-dependent texture formation, where the deposition process was performed in a cycled regime (Table 1). The cycle consisted of two equivalent steps with inverted order of the steps within the cycle. The XRD spectra of the films nucleated at the low-pressure conditions exhibited an increase, sometimes dramatic, in the volume share of the (111) oriented grains (sample A in Table 1, also Fig. 6). In contrast to this, the nucleation step occurring at the higher pressure led to a dominance in the (110) grains (sample B). It should be kept in mind that a thin layer of amorphous silicon was always pre-deposited onto the oxide surface before starting the poly-Ge$_x$Si$_{1-x}$ deposition (see the experimental section).

For the explanation of the pressure-dependent nucleation we developed a nucleation model, which was only intended for a qualitative description. The model is based on the diamond lattice features. The surface migration is not taken into account because of the low deposition temperature. Since the poly-Ge$_x$Si$_{1-x}$ has a diamond lattice, various distances between adjacent atoms characterise the atomic planes facing from both (111)- and (110)-oriented grains. For example, Sze [17] states that in the diamond lattice the (111)-planes are more closely packed than the (110)-planes. Therefore, the mean distance between atoms belonging to the (111)-plane is large than in the (110)-plane, because of the same density of the material. Indeed, one can simply derive using elementary
geometry rules that the formation of a two-dimensional (110) nucleus requires a closer-adsorbed adjacent species in the plane. Let us now consider a space containing gas-phase molecules and a surface. It is clear that the frequency of molecular impinging with the surface becomes higher with increasing the gas pressure. Some of these collisions result in an adsorption. Apparently, the adsorption time is not zero. So with rising the pressure, the density of the adsorbed species increases. This causes smaller distance between the species, which can favour the formation of the (110) nucleus with respect to the (111) nucleus.

On the basis of the assumptions proposed, a computer code has been realised. The program calculates distances between the surface species after a number of randomised adsorption acts. The relative amount of certain nucleated grains is defined as a share of the species adsorbed within a proper distance. Fig. 7 shows the result of the simulation. One can see that the dominance of the far-adsorbed species disappears at higher pressures.

The high-temperature annealing steps are included in standard CMOS processing. Since the deposition temperature, employed in this work, is much lower than the annealing temperatures, significant impact on the film texture can be expected after annealing. To investigate this, a 30-min post-anneal at 800 °C in a dry-N₂ ambient was applied to some of the samples. It has been found for the layers with a low amount of the amorphous phase that annealing could only slightly influence the film texture. In opposite to this, annealing of the semi-amorphous material resulted in a dominant crystallisation of the (111) grains. The grain size increased dramatically.

CONCLUSIONS

This work was mainly intended for a study of LPCVD of GeₓSi₁₋ₓ (X=0.3-0.65) films at a low deposition temperature of 430 °C. The following results have been found. First, the deposition rate increased with increasing Germanium content in the layers, due to an enhancement of the hydrogen desorption. This tendency was described by a gradual composition-dependent behaviour for the Germanium content below 50 atomic percent, and by an avalanche enhancement of the deposition rate for the Germanium content increasing beyond 50 atomic percent. Second, a relative GeH₄ depletion from the source mixture resulted in changing the germane-to-silane partial pressure ratio along the precursor-drift direction. The gas consumption model has been introduced, which showed a good agreement with the experimental results. Third, the polycrystalline layers mainly contained (111)- and (110)-oriented crystal grains with its ratio depending on both deposition pressure and film thickness. A rise of the pressure caused an increasing share of the (110) grains due to nucleation matters. The nucleation model was successfully introduced in order to explain a pressure-dependent nucleus formation.

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REFERENCES


FIGURES

Fig. 1. Dependence of deposition rate on germanium content for Ge$_x$Si$_{1-x}$ films deposited at 430 °C. Total pressures, Pa: (1) – 9, (2) – 20, (3) – 65.

Fig. 2. Dependence of germanium content on GeH$_4$-share in the gas phase for Ge$_x$Si$_{1-x}$ films deposited at 430 °C. Total pressures, Pa: (1) – 65, (2) – 20.
Fig. 3. Simulated GeH₄-share distributions in the downstream direction at 430 °C. Total pressures, Pa: (1, 3) – 150, (2, 4) – 20. GeH₄-flow rates, sccm: (1, 2)– 37, (3, 4) – 9.

Fig. 4. Experimental and simulated deposition-rate distributions in the downstream direction at 430 °C, $P_{tot}$ 20 Pa, and GeH₄-flow rate 37 sccm.

Fig. 5. Typical XRD spectra of thin 100-nm (lower curve) and thick 520-nm (upper curve) poly-Ge₀.₃₇Si₀.₆₃ films.

Fig. 6. XRD spectra of the films obtained after cycled deposition performed at 430 °C (see Table 1).

Fig. 7. Percentage of certain-oriented nuclei versus number of adsorption acts per time unit.

Table 1. Characteristics of many-step deposition processes for GeₓSi₁₋ₓ films deposited at 430 °C, 9 sccm GeH₄ and 21 sccm SiH₄.
**Keywords:** LPCVD, Germanium-Silicon, germane, silane.