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In-situ Doping of LPCVD Poly Silicon (II)

Temperature Influence

Poly silicon deposition by pyrolysis of silane under low pressure conditions has been investigated with respect to the influence of temperature when simultaneously in-situ doping of the deposited layer takes place.

The growth rate of poly silicon is retarded in the presence of phosphine provided that a certain lower PH_3/SiH_4-ratio has been exceeded. It has been shown how that lower ratio depends on temperature.

Increasing PH_3/SiH_4-ratio not only slows down layer growth rate but also the apparent activation energy of the layer forming reaction. An empirical equation describing the temperature dependence of that activation energy has been derived. Phosphine adsorption has been discussed as a cause of both layer growth rate and activation energy reduction. Additionally, incorporation of phosphorus during layer growth has been investigated with respect to the total amount and the electrically active concentration, the latter measured after a postdeposition anneal at 1000 °C.

Es wird die Siliciumabscheidung durch Pyrolyse von Silan unter reduziertem Druck im Hinblick auf die Temperaturabhängigkeit bei gleichzeitiger in-situ Dotierung der Schicht untersucht. Die Abscheidungsrate des Siliciums wird bei Anwesenheit von Phosphin herabgesetzt, wenn ein bestimmter unterer Grenzwert des PH_3/SiH_4-Verhältnisses überschritten wird. Die Temperaturabhängigkeit dieses Grenzverhältnisses wird nachgewiesen. Durch ein zunehmendes PH_3/SiH_4-Verhältnis wird außer der Schichtwachstumsrate auch die Größe der scheinbaren Aktivierungsenergie des Schichtbildungsprozesses herabgesetzt. Es wird eine empirische Gleichung hergeleitet, welche diesen Einfluß beschreibt. Die Adsorption von Phosphin wird als eine mögliche Ursache für die Herabsetzung sowohl der Wachstumsrate als auch der Aktivierungsenergie diskutiert. Zusätzlich wird auch der während des Schichtwachstums stattfindende Phosphoreinbau untersucht und in Bezug auf den Gesamteinbau und den elektrisch aktiven Anteil, wobei letzterer nach einer Aktivierungstemperatur bei 1000 °C gemessen wurde, ausgewertet.

1. Introduction

In Part (I) of the paper the authors reported on investigations concerning the deposition of in-situ phosphorus-doped poly silicon layers on smooth wafer surface as well as within reactive-ion-etched small trenches. It was observed that different PH_3/SiH_4-ratios of the reaction gas influence the growth rate of poly silicon not only on the planar wafer surface but also on trench walls. Both effects are characterized by a growth rate retardation, its degree, however, is different, though it is clearly determined by the amount of PH_3/SiH_4-ratio.

The present paper mainly deals with the influence of temperature on the growth of in-situ phosphorus-doped poly silicon. Silicon is deposited, as it is the common use, by pyrolysis of silane at processing temperatures covering the range from 625 °C to 830 °C. Pyrolysis of silane is commercially carried out at both higher and lower temperatures as well. When processing temperatures were chosen sufficiently high, silicon will grow forming an epitaxial layer. On the surface of amorphous films or at sufficient low temperature polycrystalline layers are formed. At temperatures below 620 °C amorphous silicon films will grow.

However, not only layer consistency but also the amount of layer growth rate is a function of temperature. The effect of temperature on layer growth is characterized by the amount of the apparent activation energy of the silicon deposition reaction. For this quantity values have been reported that covers the range from about 5 kcal/mole to about 60 kcal/mole. Recently they were summarized by Buss et al. as well as Robbins and Young. In the case of poly silicon the published data determined by growth rate evaluation, gather round $34 \leqq (E_a)_{Si} \leqq 38$ kcal/mole. In the case of in-situ phosphorus-doped poly silicon Learn and Foster obtained 46 kcal/mole and Harbeke et al. 44.6 kcal/mole. The latter authors specified their findings by relating it to certain amounts of PH_3/SiH_4-ratio, silane flux, total pressure and wafer spacing.

Supposing the experimentally observed apparent activation energy to be a composite quantity that represents more than a single reaction step, its changing amounts should not be against all expectations. Beside temperature that activation energy may possibly depend on other special process parameters, too.

It is the concern of the present paper to inform of investigation results that show the real amount of the apparent activation energy characterizing in-situ doped poly silicon deposition, to be additionally effected by the PH_3/SiH_4-ratio of the reaction gas.

The presented results also include the effect of processing temperature on the content of both total and electrically active phosphorus in the poly silicon layer. Total concentrations of phosphorus have been obtained from SIMS-measurements, those of electrically active phosphorus by applying a four-point-probe technique suited for measuring sheet resistances, after a 1000 °C-anneal had been carried out. Layer thicknesses have been measured by the use of ellipsometric as well as IR-spectroscopic methods.

It is a particular intention of the present work to investigate poly silicon deposition under the condition of in-situ doping not only on planar surfaces of silicon wafers but also within small trenches etched down from wafer surface. It should be of common interest to know about the temperature dependence of layer growth retardation within trenches. Unfortunately, our prepared examples, with respect to this aim, did not show a sufficient enough usability.

2. Experiments

In contrast to serious scientific investigations technology-related work is often carried out by using conventional production-line equipment. So in our work a commercial LPCVD hot-wall reactor has been used, the interior walls of which were covered with deposits caused by previous processing cycles. Deposition already takes place within the entrance part of the reactor tube, by which the gas composition is altered. Total pressure regulates itself by the amount of gas input on the one hand and the constant speed of the vacuum pumping system on the other. Total pressure varied within 0.2 – 0.4 Torr for all the experiments considered here. Silane input was about 200 sccm/min and pure phosphine input in the range from 0.03 – 15 sccm/min. Deposition temperature has been varied from 625 °C to 830 °C, it was measured by applying a thermocouple scratching along the wall of the wafer loaded and evacuated reaction tube. Partly, temperature was varied by adjusting various flat temperature levels, and partly by adjusting steep temperature profiles selecting correspondent wafer positions for evaluation. All depositions were done by applying a wafer cage, the wafers spaced 11 mm apart. The clearance of the cage was 88 mm, wafer diameter 76 mm. Poly silicon was deposited on 80 nm thick, thermally grown silicon dioxide with layer thickness ≧ 400 nm. The sheet resistance was measured after a post-deposition anneal that includes a 10 min oxidation step in dry oxygen at 900 °C followed by a 20 min ramp up to 1000 °C, a 20 min stay at that temperature and a 20 min ramp down to 900 °C in dry nitrogen.

3. Results and discussion

Poly Silicon LPCVD layer growth will be discussed with respect to the effect of temperature on growth rate retardation caused by phosphorus in-situ doping of the layer. In completing the results layers are studied with regard to temperature influence on incorporation as well as distribution of phosphorus in the layer with respect to electrically active and total concentrations.

3.1. Layer growth rate behaviour

It is a commonly accepted fact that in-situ doping, under certain circumstances, extremely alters layer growth rate of deposited poly silicon. Growth rate is enlarged by diborane and retarded by phosphine or arsine in the reaction gas, provided a certain dopant source to silane ratio has been exceeded. Below that certain ratio poly silicon growth rate is not effected by the presence of dopant sources in the gas.

The effect of phosphine added to silane on layer growth rate disappears not only with respect to small PH_3/SiH_4-ratios but also with respect to great PH_3/SiH_4-ratios, as can be seen from LEARN's data (shown there in Figure 3). The medium range of PH_3/SiH_4-ratios ($2 \cdot 10^{-2} > PH_3/SiH_4 > 4 \cdot 10^{-4}$), however, bears a great resemblance to a hyperbolic course. It can be changed into a quasilinear graph by plotting the reciprocal growth rate data versus the data of logarithmated PH_3/SiH_4-ratio, what is shown in Figure 1.

The left hand data related to 800 °C and 770 °C, respectively, illustrate how the PH_3/SiH_4-effect flattens at PH_3/SiH_4-ratios high enough. The 700 °C and the 640 °C related data indicate how far the quasilinear relation may be extended. The remaining data (670 °C and 656 °C) were taken from CHANG, they illustrate first of all, the presence of constant growth rate levels at PH_3/SiH_4-ratios small enough.

The data related to 700 °C and 640 °C, respectively, confirm the parallel displacement of the function along the abscissa when silicon deposition temperature is changed. Taking the interceptions on the axis of abscissa as a rough measure for the transition from phosphine-effected layer growth to uneffected growth conditions, a temperature dependence of that transition can be discussed. Figure 2 contains an Arrhenius plot of the abscissa interception data characterized by an apparent activation energy of $(E_a)_{P/Si} = 44$ kcal/mole.

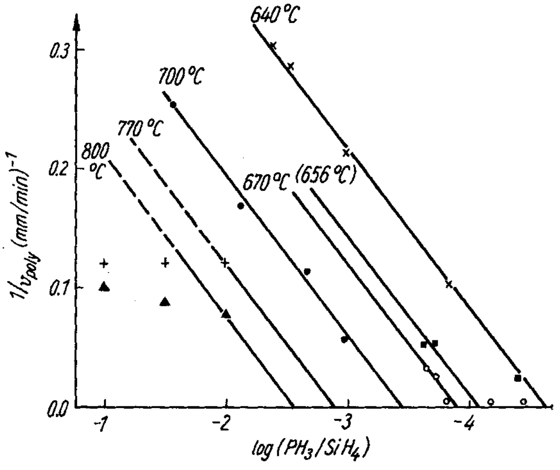

Fig. 1. Representation of in-situ phosphorus doped poly silicon growth rate versus phosphine to silane ratio of the reaction gas and deposition temperature as the parameter. Data for 670 °C and 656 °C were taken from CHANG (▲ 800 °C; + 770 °C; ● 700 °C; ○ 670 °C; ■ 656 °C; × 640 °C)

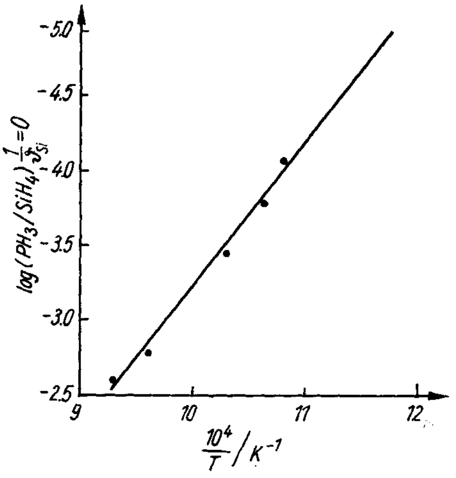

Fig. 2. Arrhenius plot of the abscissa interceptions from Figure 1 taken as a measure of the transition from phosphine-retarded to unretarded poly silicon layer growth

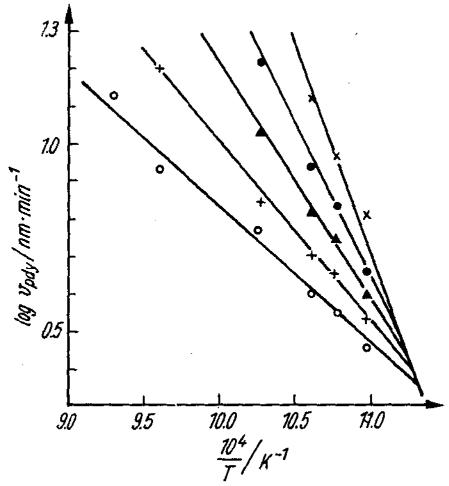

Fig. 3. Arrhenius plot of layer growth rate with log (PH_3/SiH_4) as the parameter, exposing the different degree of temperature influence. Data were taken from the linear parts of Figure 1 (log PH_3/SiH_4: ○ −2.0; + −2.4; ▲ −2.75; ● −3.0; × −3.3)

On the background of Figure 2 uneffected layer growth should be expected at 600 °C, when $PH_3/SiH_4 < 3 \cdot 10^{-5}$ are applied, and at 800 °C, when $PH_3/SiH_4 < 2.5 \cdot 10^{-3}$ are used. Additionally that transition might be influenced by total pressure and hydrogen/silane-ratio, too.

The temperature dependence of poly silicon growth rate can be obtained from the data drawn up in Figure 1. For this purpose different Arrhenius plots have to be drawn with the PH_3/SiH_4-ratio as a parameter. Figure 3 shows such an arrangement. It reveals the fact that the apparent activation energy of poly silicon deposition (given by the slope of each Arrhenius straight line) grows smaller with the PH_3/SiH_4-ratio increased.

The amount of the apparent activation energy follows the PH_3/SiH_4-ratio in the form of an exponential function as is illustrated by Figure 4. Fortunately, HARBEKE et al. had published data on the temperature dependence of insitu phosphorus doped poly silicon

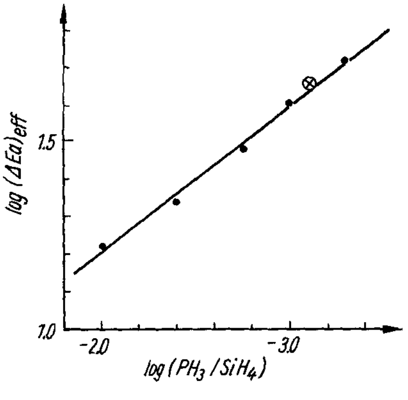

Fig. 4. Representation of activation energy dependence on PH_3/SiH_4-ratio according to Figure 3. × Measuring point given by HARBEKE et al.

together with specified PH_3/SiH_4-ratio. Those values agree fairly well with the course given in Figure 4. The course of Figure 4 is determined by an empirical function that reads as follows:

$$(E_{aSi})_{eff} = 2.5 \cdot 10^3 \cdot (PH_3/SiH_4)^{-0.4} \tag{1}$$

According to equ. (1) the hight of the energy barrier of silicon deposition will change from $(E_{aSi})_{eff} = 57$ kcal/mole at the transition to uneffected layer growth ($PH_3/SiH_4 \leqq 4 \cdot 10^{-4}$) to $(E_{aSi})_{eff} = 16$ kcal/mole at $PH_3/SiH_4 = 10^{-2}$.

Deposition of undoped polycrystalline silicon under conditions similar to that of in-situ doped silicon yielded a temperature effect characterized by $(E_{aSi})_{eff} = 34$ kcal/mole, which amount agrees with that observed previously by EVERSTEIJN and PUTT, who investigated atmospheric pressure CVD with hydrogen as carrier gas and silane as well as silicon chlorides as the source gases. They obtained $(E_{aSi})_{eff} = 36-37$ kcal/mole. The latter value has been confirmed by SCOTT et al., who investigated heterogeneous poly silicon growth in a temperature range below 560 °C, gas phase reactions were suppressed by performing all experiments at very short gas residence times and very low total pressure. ROBERTSON et al., however, observed an activation energy as high as $(E_{aSi})_{eff} = 56$ kcal/mole, what result, in the opinion of SCOTT et al., should be associated with a homogeneous reaction that decomposes silane partly forming silylene:

$$SiH_4 \rightarrow SiH_2 + H_2 + 55.9 \text{ kcal/mole} \tag{2}$$

Reaction (2) should be promoted by high total pressure of silane (ca. 1 Torr) and, in consequence, by a high residence time of silane in the reactor chamber. BUSS et al., at least, observed a reaction barrier hight $(E_{aSi})_{eff} = 55-60$ kcal/mole for heterogeneous silane decomposition on a silicon surface from molecular-beam related experiments and suggested dehydrogenation of adsorbed silylene as the reaction controlling step.

$$SiH_2{*} \rightarrow Si + H_2 + {*} + 59 \text{ kcal/mole} \tag{3}$$

So, the reaction equations (2) and (3) might characterize an alternating path of forming silicon from silane, which, in contrast to a one step decomposition (cp.equ (4)) is characterized by a high reaction barrier.

$$SiH_4 \rightarrow Si + 2\,H_2 \tag{4}$$

Our results, however, show a decreasing activation energy of silicon deposition with the PH_3/SiH_4-ratio increased. A positive activation energy should, in general, cause the reaction rate to be increased. In the case of in-situ phosphorus doped poly silicon, however, the decreasing activation energy is associated with a decrease of layer growth rate. To understand this fact we should remember the adsorption behaviour of phosphine on silicon surface which had been intensively studied by YV et al. Consequently, phosphine molecules will be adsorbed without effective dissociation and desorption of hydrogen below a temperature of 400 °C. Four surface silicon atoms will be occupied by only one phosphine molecule. Above 400 °C hydrogen desorption indicates active dissociation of phosphine in consequence of which, indeed, more phosphine can be adsorbed till close to phosphorus monolayer formation at 550 °C. Phosphorus coverage decreases more and more when temperature is further increased. In consequence, retardation of poly silicon layer growth caused by phosphine follows the coverage of the surface with hydrogen and phosphorus as well as the bonding strength of chemisorption. From this point of view higher temperatures coupled with a higher phosphine input that should be necessary for a certain level of phosphorus doping of the layer, should be expected more advantageous than a lower phosphine input coupled with a lower process temperature.

In order to adjust a sufficient high growth rate, PH_3/SiH_4-ratio has to be decreased or temperature increased, for instance, in accordance with Figure 1. Figure 3, however, is more suited to give a rough idea of how PH_3/SiH_4-ratio effects layer growth rate. Figure 3 implies the ansatz that reads as follows:

$$V_{Si} = (V_{Si})_0 \cdot \exp - \frac{(E_{a\,Si})_{eff}}{R_T} \tag{5}$$

Equ. (5) in its logarithmated form approaches the experimental relation V_{Si} (T; PH_3/SiH_4) by inserting empirical coefficients and taking into account equ. (1):

$$\log V_{Si} = \frac{0.834}{(PH_3/SiH_4)^{0.36}} = \left[1 - \frac{0.0652}{(PH_3/SiH_4)^{0.04}} \cdot \frac{10^4}{T}\right] \tag{5a}$$

3.2. Phosphorus content of the layer

The purpose of in-situ doping of poly silicon layers is to suppress a postdiffusion step and, in consequence, the associated temperature-time charging of the whole structure. Unfortunately the well known relationships of epitaxial silicon between incorporated dopants and layer resistivity are not applicable to poly silicon.

Comparable conductivity values are obtained not till doping level exceeds 10^{18} cm^{-3}. In Part (I) of the paper process control of electrically active phosphorus in in-situ doped poly silicon layer with respect to PH_3/SiH_4-ratio of the gas has been studied for a process temperature of 700 °C. The full line of Figure 5 illustrates the effect of deposition temperature on the concentration of electrically active phosphorus for a constant PH_3/SiH_4-ratio of $2.3 \cdot 10^{-2}$. All the samples had seen a postanneal at 1000 °C before sheet resistances were measured. Poly silicon grain growth had not been investigated neither after layer deposition nor after activation anneal.

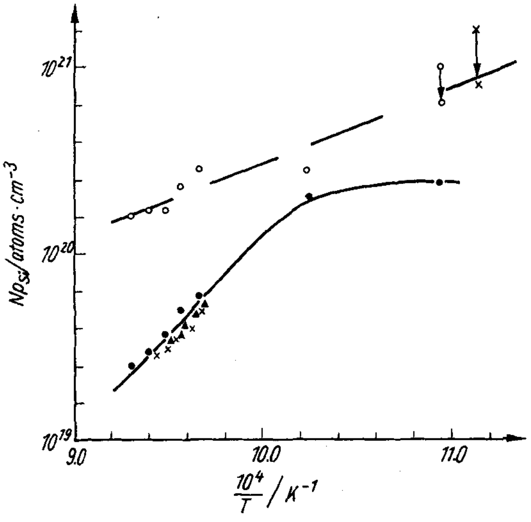

Fig. 5. Arrhenius plot of the phosphorus content of poly silicon layer for $PH_3/SiH_4 = 2.3 \cdot 10^{-2}$; V_{SiH_4} = 214 sccm/min. Full line: electrically active phosphorus content obtained by sheet resistance and layer thickness measurement and applying ASTM conversion curve); Dashed line; total phosphorus content (obtained by SIMS); right hand data-points were taken from Learn and Foster and converted to the related gas composition

Additionally, Figure 5 shows the total content of phosphorus in the layer as has been observed by SIMS. The two right hand points have been converted to the special gas conditions the figure is related to. Total phosphorus content is characterized by a weaker dependence on temperature in comparison with the electrically active phosphorus. The concentration of the latter, however, tends to saturate in the range of lower deposition temperatures. So, a total phosphorus content in the range of $10^{20}-10^{21}$ cm^3 should contribute to layer conductivity the best in the vicinity of a deposition temperature of 700 °C.

4. Conclusions

Growth rate of LPCVD poly Silicon is retarted in the presence of phosphine during silicon deposition when a certain lower value of the PH_3/SiH_4-ratio is exceeded. The amount of that critical ratio depends on temperature. The effect of temperature on layer growth rate is influenced by the amount of PH_3/SiH_4-ratio, in consequence a PH_3/SiH_4-ratio dependent activation energy has been obtained. Layer growth rate decreases when PH_3/SiH_4-ratio is enlarged, though activation energy simultaneously grows smaller. That can be explained by taking into account the adsorption sites blocking function of phosphine. At constant PH_3/SiH_4-ratio the more phosphorus will be in-situ incorporated during layer growth the lower deposition temperature has been chosen. From our findings, however, it should be concluded that layer conductivity, as can be observed after an activation anneal at 1000 °C, will be the best when layer deposition takes place in the vicinity of 700 °C.

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