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# Boron Doping Effect on Silicon Film Deposition in the Si<sub>2</sub>H<sub>6</sub>-B<sub>2</sub>H<sub>6</sub>-He Gas System

Satoshi Nakayama, Izumi Kawashima, and Junichi Murota<sup>1</sup>

Nippon Telegraph and Telephone Corporation, Atsugi Electrical Communication Laboratories, Atsugi, Kanagawa, 243-01 Japan

#### ABSTRACT

Heavily boron-doped silicon films are deposited in the temperature range  $520^{\circ}$ - $665^{\circ}$ C in the Si<sub>2</sub>H<sub>6</sub>-B<sub>2</sub>H<sub>6</sub>-He gas system. The effects of boron doping on the deposition rate and properties of silicon films are investigated and compared with those of phosphorus doping. The deposition rate increases with the addition of B<sub>2</sub>H<sub>6</sub>, and the deposition rate increment is proportional to <sup>3</sup>/<sub>3</sub> power of the boron concentration in silicon film and to the partial pressure of Si<sub>2</sub>H<sub>6</sub>. Boron is deposited independently without the influence of silicon deposition. The amorphous-crystalline transition temperature is decreased with incorporating boron in silicon film except for the higher boron concentration than  $2 \times 10^{20}$  cm<sup>-3</sup>. For the higher boron concentration, crystallization is suppressed by incorporating boron.

Heavily doped polycrystalline silicon film is an important material as a gate electrode of MOSLSI's. When polycrystalline silicon film is used as a gate electrode of MOSLSI's, it is generally deposited without impurity and is subsequently doped by thermal diffusion or by ion implantation of impurity. For thermal diffusion, a high temperature is necessary to obtain a low resistance. For doping by ion implantation, silicon film thickness cannot be reduced to prevent impurity penetration into the gate oxide. So, impurity doping, especially, boron doping during film deposition, is useful for submicron P channel MOSFET's in CMOSLSI's.

Generally, silicon films have been deposited by thermal decomposition of SiH<sub>4</sub>. For the SiH<sub>4</sub> gas system, the effects of impurity doping on the growth rate and properties of silicon films are well known. For instance, the deposition rates of silicon films decrease with the addition of  $PH_3$ , (1, 2), and increase with the addition of  $B_2H_6(1, 3)$ . Recently, we have reported that  $Si_2H_6$  is suitable as a source gas to prepare heavily phosphorus-doped polycrystalline silicon film because the deposition rate is not influenced by the addition of PH<sub>3</sub> and is about 100 times or more higher than that for the SiH<sub>4</sub> gas system (4). For the  $Si_2H_6$  gas system, however, there is little data about the effects of boron doping on the deposition rate and properties of silicon films. In this paper, the relationships between the deposition rate of silicon films and  $B_2H_6$  partial pressure or boron concentration in silicon films, the heat-treatment temperature dependencies of crystallization, and resistivity of boron-doped silicon films are described and compared with those for the addition of PH<sub>3</sub>.

### **Experimental Procedure**

Silicon films were deposited under low pressure in a lamp-heated horizontal reactor using the Si<sub>2</sub>H<sub>6</sub>-B<sub>2</sub>H<sub>6</sub>-He gas system. The deposition temperature range was 520°-665°C, the deposition pressure was about  $4 \times 10^{-3}$ atm, and the deposition thickness was 3000-5000Å. The substrates used were p-type silicon wafers with mirrorpolished (100) surfaces. An oxide film was thermally grown on the substrates in an atmosphere of dry O<sub>2</sub> gas before the silicon film was deposited. The samples were heat-treated for 30 min at 575°-1050°C in a dry N<sub>2</sub> atmosphere.

The concentration of boron in silicon film was determined by secondary ion mass spectrometry. The gas phase composition in the reactor was investigated by

Present address: Research Institute of Electrical Communication, Tohoku University, Sendai, Miyagi, 980 Japan.

quadrapole mass spectrometry. The other experimental procedure has been described elsewhere (4).

### **Results and Discussion**

Deposition rate and boron concentration in silicon film.-Figure 1 shows the deposition temperature dependences of silicon film deposition rate (R). The deposition rate is increased even by the slight addition of  $B_2H_6$ , while it is not influenced by the addition of PH<sub>3</sub>. The apparent activation energy of deposition rate for borondoped silicon film is less than that for undoped silicon film which is about 40 kcal/mol. It should be noted that the increment of deposition rate with the addition of  $B_2H_6$  is influenced little by the deposition temperature.

Figure 2 shows the dependence of boron concentration  $(C_B)$  on the B<sub>2</sub>H<sub>6</sub> partial pressure in the gas introduced into the reactor  $(P_{B_{2H_6}})$ .  $C_B$  increases with increasing  $P_{B_{2H_6}}$ and is inversely proportional to  $P_{\text{SigH}_6}$ . Boron was incorporated beyond  $1 \times 10^{22}$  cm<sup>-3</sup> for above  $P_{\text{BgH}_6}$  of  $5 \times 10^{-6}$  atm and below  $P_{\text{SigH}_6}$  of  $1.2 \times 10^{-4}$  atm, while phosphorus was not incorporated beyond  $2 \times 10^{21}$  cm<sup>-3</sup> as reported elsewhere (4). Furthermore, it was confirmed that boron is deposited on silicon by the decomposition of  $B_2H_6$ 





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Fig. 2.  $P_{\rm B_{2}H_{6}}$  dependence of boron concentration

even at  $P_{\text{SigH_6}} = 0$  atm. The doping velocity, *i.e.*, incorporated flux of boron into the silicon film, which is defined by the product of  $C_B$  and R ( $C_B \times R$ ), is proportional to  $P_{\text{B_2H_6}}$  and independent of  $P_{\text{SigH_6}}$  as shown in Fig. 3. Therefore, it is considered that boron is deposited independently without influence of silicon deposition in the Si<sub>2</sub>H<sub>6</sub>-B<sub>2</sub>H<sub>6</sub>-He gas system. Furthermore, the doping velocity of boron was dependent on gas flow velocity in the reactor, and the activation energy of  $C_B \times R$  in the temperature range 550°-630°C was about 9 kcal/mol, whose value shows that doping velocity is little dependent upon temperature in the present condition. Therefore, it is considered that the incorporation of boron into silicon film is controlled by the diffusion of molecules including boron in the gas phase.

Influence of boron on deposition rate of silicon film.— For the higher  $P_{\text{B2H6}}/P_{\text{Si2H6}}$  than  $2 \times 10^{-3}$ , the film thickness has lost uniformity, and the deposition rate and boron concentration were not able to be treated quantitatively. Therefore, we discuss the influence of boron on the deposition rate of silicon film under the condition that the boron concentration is below  $1 \times 10^{21}$  cm<sup>-3</sup>.

1016

sizHe (atm)

Under the present condition, the deposition rates of undoped silicon films at constant  $P_{\rm Si_2H_6}$  were independent of the gas flow velocity and total pressure in the reactor. From these results, it is considered that the deposition rates of these silicon films are controlled by the surface reaction. It was also confirmed by the quadrupole mass spectrometer that SiH<sub>4</sub> is generated during the deposition of undoped silicon film from Si<sub>2</sub>H<sub>6</sub>, and the amount of SiH<sub>4</sub> generated is independent of the gas flow velocity. These results suggest that the following reaction [1], which is the same as the initial step in the thermal decomposition of Si<sub>2</sub>H<sub>6</sub> in the gas phase (5), occurs on the surface of silicon film

$$Si_2H_6 \rightarrow SiH_4 + SiH_2$$
 [1]

For the addition of  $B_2H_6$ , the deposition rate increased and was dependent on the gas flow velocity and total pressure in the reactor. As a result of the measurement of gas phase composition in the reactor by the quadrupole mass spectrometer, Si-B compounds were not observed in the gas phase and the intensity of  $B_2H_6$  was independent of  $P_{\text{SigHg}}$ . From these results, it is expected that the deposition rate is not influenced by gas phase reaction and  $\text{Si}_2H_6$  decomposes on the silicon surface. Thus, it is considered that the dependence of deposition rate on the gas flow velocity and total pressure in the reactor results from alteration of the surface reaction due to incorporation of boron, because the boron doping velocity is dependent on the gas flow velocity as described in the previous section.

From this discussion, it is assumed that the deposition rate of boron-doped silicon film (*R*) is expressed by the sum of undoped deposition rate term ( $R_0$ ) and additional deposition rate term (dR), which is a function of  $C_B$  and  $P_{Si_2H_6}$ . Under the present condition, the deposition rate of undoped silicon film was proportional to  $P_{Si_2H_6}$ . *R* is written as follows

$$R = R_0 + dR$$
 [2]

$$R_0 = k_0 P_{\rm Si_2H_6}$$
 [3]

$$dR = kC_{\rm B}{}^{m}P_{\rm SigHg}{}^{n}$$
<sup>[4]</sup>

where  $k_0$  and k are the rate constants of undoped deposition rate and additional deposition rate, respectively, and m and n are index numbers. From Eq. [2], [3], and [4]

$$dR/R_0 = k/k_0 * C_B^m P_{Si_2H_6}^{n-1}$$
[5]

The dependence of dR/R on  $C_{\rm B}$  is shown in Fig. 4. dR/R is proportional to  $C_{\rm B}^{2/3}$  regardless of  $P_{\rm Sl_2H_6}$ . From Fig. 4, m and n are determined to be  $\frac{3}{3}$  and 1, respectively, *i.e.* 





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Table I. The total amount of <111>, <110>, and <311> textures of silicon measured by x-ray diffraction for the film deposited at 575°C

С <sub>в</sub> (ст <sup>-3</sup> )	Heat-treatment temperature (°C)				
	As-depo	575	600	625	650
Undoped	*	*	*	3	23
$4.8 \times 10^{18}$	*	*	*	1	18
$1.4 \times 10^{19}$	*	*	13	12	15
$8.0 \times 10^{19}$	*	16	18	16	18
$1.9 \times 10^{20}$	*	14	18	17	15
$1.6 \times 10^{21}$	*	*	*	*	6
$6.7 \times 10^{21}$	*	*	*	*	*

\* Undetected.

where  $k_0 = 3.2 \times 10^6$  Å/min/atm,  $k = 7.5 \times 10^{-8}$  Å/min/atm at 575°C. The activation energy of  $k_0$  is about 40 kcal/mol and that of k is small (~0 kcal/mol). This equation means that  $C_{\rm B}$  increases but R decreases with decreasing  $P_{\rm Si_2H_6}$ , because the increment of  $(k_0 + kC_{\rm B}^{23})$  for reduced  $P_{\rm Si_2H_6}$  is no so much as the amount of  $P_{\rm Si_2H_6}$  reduction. Considering that  $C_{\rm B}^{23}$  is proportional to the surface density of boron, it is suggested that reaction [1] is enhanced on the adsorption site composed of deposited boron.

Property of silicon film deposited from Si<sub>2</sub>H<sub>6</sub>.-To investigate the film structure, x-ray diffraction was used. Only (111), (220), and (311) peaks of silicon were observed. To evaluate the relative amount of <111>, <110>, and <311> textures, x-ray diffracted intensities of (111), (220), and (311) peaks were measured and divided by the correction factors, 1.00, 0.37, and 0.18, respectively. The x-ray diffracted data showed that the silicon films after heat-treatment preferred weakly <111> orientation. The total amount of <111>, <110>, and <311> textures of silicon films after heat-treatment are listed in Table I for the films deposited at 575°C ( $I_{x-ray}$ ). As-deposited silicon films are amorphous-like regardless of boron concentration. From Table I, it is found that the undoped silicon film is crystallized with the heattreatment for 30 min at about 650°C. The amorphouscrystalline transition temperature is the same as for the CVD silicon film deposited from SiH4 reported by Nagasima et al. (6). Except for the silicon film with high boron concentration above  $1.6 \times 10^{21}$  cm<sup>-3</sup>, the amorphouscrystalline transition temperature is decreased by incorporating boron in silicon. It has been reported by Mei et al. that the grain growth of polycrystallite silicon film is not enhanced by incorporating boron (7). And it is well known that crystallization in amorphous materials occurs through the nucleation of crystallites and their subsequent grain growth of crystallites formed during the nucleation (8). From the  $C_B$  dependencies of  $I_{x-ray}$  shown in Table I, it is considered that nucleation is enhanced by incorporating boron except for above  $1.6 \times 10^{21}$  cm<sup>-3</sup>.

For the higher concentration of boron than  $1.6 imes 10^{21}$ cm<sup>-3</sup>, diffracted intensity is much lower than that for the undoped silicon film. Even after heat-treatment at higher temperature (900°C), x-ray diffracted peaks of silicon were very small and broad. This indicates that crystallization is suppressed by incorporating boron in high boron concentration film. In order to investigate the structure of high boron-doped silicon film in more detail, electron diffraction was used. Electron diffraction pattern of high boron-doped silicon film ( $C_B = 1.6 \times 10^{21}$  cm<sup>-3</sup>) annealed at 900°C is shown in Fig. 5. The electron diffraction rings are diffused. Looking at the pattern in more detail, three rings are found. The lattice constants obtained from the rings were 4.1, 2.5, and 1.4Å whose values are not in agreement with silicon lattice constants. Therefore, it is expected that these electron diffraction rings are composed of boron or Si-B compound which is  $SiB_4$  or  $SiB_6$  as reported by Arai et al. (9). Makino et al. also observed that the grain growth is suppressed for high boron-doped polycrystalline silicon ( $C_{\rm B}$ =  $3.3 \times 10^{21}$  cm<sup>-3</sup>) (10). They attributed this suppression of grain growth to the boron precipitations at the grain





Fig. 5. Electron diffraction pattern of high boron-doped silicon film after heat-treatment at 900°C.

boundary. In our experiment the formation of Si-B compound, which is expected to be  $SiB_4$  or  $SiB_6$ , or the precipitations of boron may be responsible for the suppression of crystallization of high boron concentration silicon film.

After heat-treatment above 700°C, the resistivity of film was little dependent on heat-treatment temperature. So, the dependence of film resistivity after heat-treatment at 1000°C on impurity concentration was investigated. The results are shown in Fig. 6 together with the phosphorus doped polycrystalline silicon data reported elsewhere (4). For the boron-doped silicon film, the resistivity is minimum at  $C_B = 2 \times 10^{20}$  cm<sup>-3</sup>. Its minimum value is about  $2 \times 10^{-3} \Omega$ -cm. The increase of the resistivity in the boron concentration range above  $C_B = 2 \times 10^{20}$  cm<sup>-3</sup> may result from the formation of Si-B compound or precipitation of boron as discussed above. For the phosphorus-doped silicon film, the minimum resistivity is about  $5 \times 10^{-4} \Omega$ -cm at about phosphorus concentration ( $C_P$ ) of  $1 \times 10^{21}$  cm<sup>-3</sup>. The dependence of resistivity on the impurity

Heat-Treatment  $10^{-1}$   $10^{-2}$   $10^{-2}$   $10^{-2}$   $10^{-2}$   $10^{-2}$   $0^{-2}$  $0^$ 

Fig. 6. Impurity concentration dependence of resistivity after heattreatment at 1000°C.

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concentration is the same as that for the silicon film deposited in the  $SiH_4$  gas system (11).

#### Conclusion

The deposition rate of silicon film in the Si<sub>2</sub>H<sub>6</sub>-B<sub>2</sub>H<sub>6</sub>-He gas system increases by the addition of  ${\bf B}_2 {f H}_6,$  which is different from the Si<sub>2</sub>H<sub>6</sub>-PH<sub>3</sub>-He gas system where the deposition rate is not influenced by the addition of PH<sub>3</sub>. The deposition rate in the Si<sub>2</sub>H<sub>6</sub>-B<sub>2</sub>H<sub>6</sub>-He system is expressed by the sum of undoped deposition rate term and additional deposition rate term which is proportional to <sup>2</sup>/<sub>3</sub> power of the boron concentration in silicon films. In the system, boron is deposited independently without influence of silicon deposition. The amorphous-crystalline transition temperature is decreased with increasing boron concentration in silicon film except for the higher boron concentration than  $1.6 \times 10^{21}$  cm<sup>-3</sup>. For the higher concentration of boron than  $1.6 imes 10^{21}$  cm<sup>-3</sup>, crystallization is suppressed by the Si-B compound formation or the precipitation of boron. The minimum value of resistivity after heat-treatment at 1000°C is  $2 \times 10^{-3} \Omega$ -cm for the boron-doped silicon film, which is 4 times higher than that for phosphorus-doped silicon film.

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# Silicon Cantilever Beams Fabricated by Electrochemically **Controlled Etching for Sensor Applications**

## P. M. Sarro and A. W. van Herwaarden

Department of Electrical Engineering, Electronic Instrumentation Laboratory, Delft University of Technology, P.O. Box 5031, 2600 GA Delft, The Netherlands

#### ABSTRACT

An electrochemically controlled etching of silicon and an integrated circuit technology are used to fabricate 10 µm thick cantilever beams containing integrated devices. Such structures are fabricated by two different methods, each of which is analyzed and the advantages and problems inherent in them stated. The influence of several parameters on the etch rate of silicon and on the quality of the beam surface is examined. Finally, an example of the application of such silicon microstructures to sensors is presented: a vacuum sensor, a novel type of thermal vacuum gauge, based on an integrated silicon thermopile.

Silicon micromachining is of great importance for the development of inexpensive, batch-fabricated, highperformance sensors that can easily be interfaced with microprocessors (1). Silicon microstructures, such as membranes and cantilever beams, are particularly important for thermal sensors (vacuum sensor (2), infrared sensor of the thermal type (3, 4), etc.), since they reduce the thermal capacity of the device and provide thermally isolated regions, thus improving the device performance

In this paper, we report on the fabrication of 10 µm thick silicon cantilever beams containing integrated devices (see Fig. 1). While cantilever beams made of SiO<sub>2</sub> or SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub>, as well as beams made of heavily doped p<sup>+</sup> silicon (used mostly as supporting structures), have been realized for several applications (1), cantilever beams made of low, uniformly doped epilayer silicon and containing integrated devices have-to the best of our knowledge-not yet been reported. These novel structures were realized using integrated circuit fabrication technology and an electrochemically controlled etching (ECE) of silicon. This ECE technique (5), in which a voltage bias on the n-type epilayer is employed to prevent the epilayer from being etched, can be performed as the last step in the fabrication process, allowing devices to be fabricated within the membrane by means of standard silicon planar technology. Other advantages offered by this combination of silicon planar technology and ECE are: batch-fabrication (with a high yield and thus low cost) and the possibility of having on-chip interface electronics.

Two methods of preparing silicon cantilever beams are described. In one method, electrically isolated regions ("channels") were created on three sides of the membrane by the deep p-type (DP) isolation diffusion. In this way, the etch stops at the epilayer/substrate junction, but continues through the isolated regions. In the other, a combination of  $\bar{ECE}$  and plasma etching of silicon is used: first, membranes are fabricated by ECE, and then a photoresist layer is deposited and patterned on the front side of the wafer. The "channels" are now etched with a plasma etch process; viz., reactive ion etching. A severe bending of beams fabricated in a first run can be observed, due to stresses introduced at the silicon/silicon dioxide interface. In order to eliminate such bending, which compromises the good performance of certain sensors, the effect of the oxide thickness and of the aluminum interconnection pattern on the flatness of the beam is investigated.

An example of the application of such silicon microstructures to sensors is provided by a vacuum sensor based on an integrated silicon thermopile developed in our laboratory (2). For a 10 µm thick cantilever beam, the thermal resistance is increased by a factor of 30 with re-

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