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Selective Boron Atomic-Layer Doping of Silicon Using an HBO_2 Source and a Thin Oxide Mask

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Selective atomic-layer doping is important for future Si complimentary MOSFETs having a precisely controlled doping profile. We show, for the first time, that a thin oxide can act as a selective adsorption mask against HBO_2. Sticking coefficient of HBO_2 on the oxide decreases with increasing substrate temperature. Following the selective adsorption, sublimation of native oxide at 800°C in a UHV results in selective atomic-layer doping since B is not desorbed from Si surface.

1. INTRODUCTION

The formation of a very thin doped layer has become increasingly attractive in Si LSI technology. It has recently been reported, for example, that a punch-through stopper or an ultra-shallow junction can be formed by atomic-layer doping [1][2]. These atomic-layer doping techniques require precise control of dopant adsorption onto the Si surface. Furthermore, for practical device applications, particular in CMOS devices, dopant atoms must be restricted to well-defined regions. However, no selective atomic-layer doping technique has ever been reported. We propose that a very thin oxide layer be used as an adsorption mask. We show here that only a small fraction of an HBO_2 flux adsorbs onto the thin oxide and that this oxide mask can be sublimated by heating in UHV, resulting in selective B atomic-layer doping.

2. EXPERIMENTS

Figure 1 shows the process flow for this doping. First, the Ishizaka-Shiraki method[3] was used to form a 0.4-nm-thick oxide layer on a (100) Si substrate. Then, the oxide on half of the wafer was removed with a HF-dip. After the sample was placed in a UHV chamber and heated to about 400 °C, HBO_2 [4] was adsorbed onto the wafer at a substrate temperature (T) ranging from RT to 700°C. Then the remaining oxide was sublimated by heating at 800 °C for 10min. Finally, a Si film was grown on the B-adsorbed Si surface by MBE at T= 400-700 °C. Boron adsorption and segregation were monitored by *in-situ* AES and characterized, after growing a Si cap layer, by SIMS.

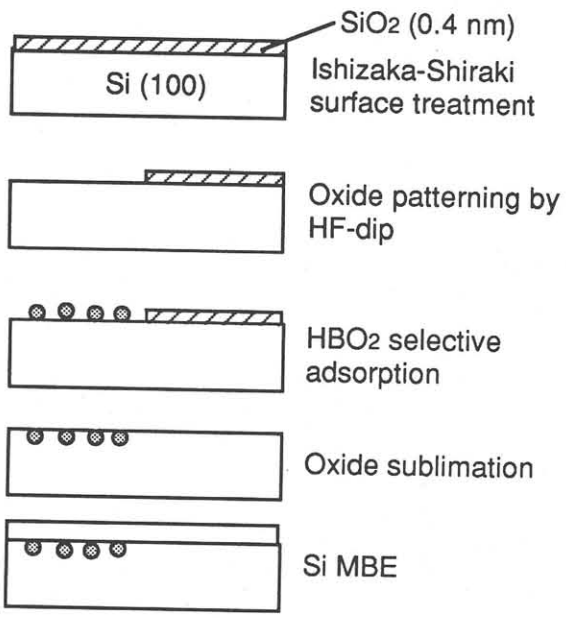

Fig. 1. Prosess flow of B selective atomic-layer doping.

3. RESULTS AND DISCUSSION

AES spectra for the Si and SiO_2 surfaces after adsorption of about 0.3 ML of HBO_2 at 600 °C are shown in Fig. 2, which shows that the boron Auger electron signal (179 eV) is observed only on the Si surface and thus that HBO_2 adsorption was very selective for that surface.

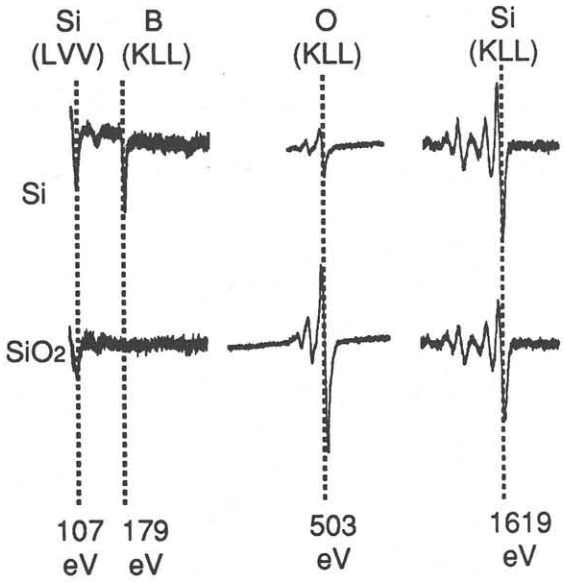

Fig. 2. AES spectra showing selective adsorption of HBO_2 on Si.

AES and SIMS were used to evaluate the temperature dependence of this selective adsorption ratio, and they revealed that HBO_2 adsorption onto Si was almost independent of temperature. The adsorption onto SiO_2, however, decreased with increasing T_{sub}. The selective adsorption ratio is therefore temperature dependent, and a high ratio of 43 was achieved at 700 °C (Fig. 3).

The temperature dependence of the sticking coefficient (S_0) of molecules like $SiCl_2H_2$ on Si surface has been discussed on the basis of the precursor-mediated adsorption model[5].

$$S_0 = \alpha / [1 + (k_d^0/k_r^0)\exp\{-(E_d-E_r)/RT\}] \quad (1)$$

α: trapping coefficient

E_d: activation energy for precursor desorption

E_r: activation energy for precursor reaction

The S_0 of B_2H_6 on Si has been shown to be very low (10^{-4} at RT), and to increase with increasing T[6]. According to equation (1), this means that the activation energy for B_2H_6 chemisorption is higher than that for desorption. In our case, S_0 of HBO_2 molecules on SiO_2 surface decreases with increasing T. This suggests that the activation energy for HBO_2 chemisorption is lower than that for desorption.

Subsequent annealing at 800 °C in UHV caused the oxygen Auger signal from SiO_2 to disappear (Fig. 4), indicating oxide sublimation. On the Si surface, however, the change in the B signal was small. This small change indicates B thermal diffusion into Si, which was confirmed by SIMS depth profiling. As a result, selective B doping was achieved. The SiO_2 pattern can be formed using excimer laser oxidation[7][8]. Moreover, this technique is free of metal contamination from the photoresist and from high energy ions. Thus, this technique is one candidate for ultraclean resistless doping.

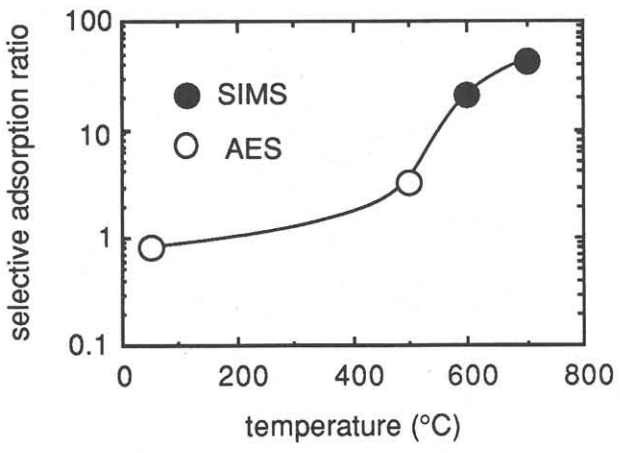

Fig. 3. Selective adsorption ratio (Si/SiO2) of HBO_2 at various substrate temperatures.

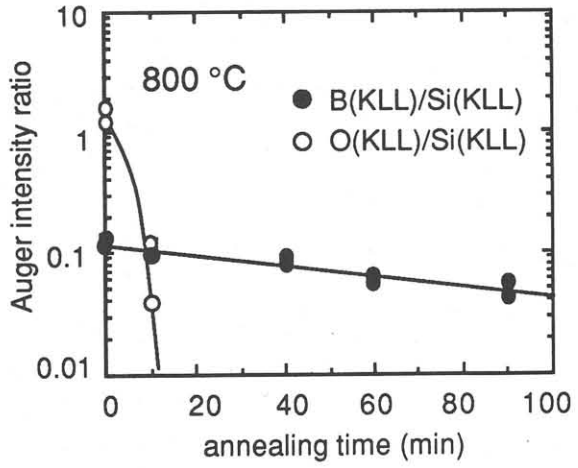

Fig. 4. AES results showing oxide sublimation and B diffusion into Si after annealing in UHV.

To form a punch-through stopper for MOSFETs, δ–doping, which is composed of atomic-layer doping and Si overgrowth, is used. Since surface segregation during Si overgrowth is the most important problem in δ–doping, it was investigated by *in-situ* AES after each sequential growth of a 2- to 5-nm thick Si layers. The decay of the B signal was found to be exponential. Arrhenius plots of the exponential decay length (segregation length), together with Nakagawa's data on Sb and Ga [9], are shown in Fig. 5. The surface segregation of B is much less than

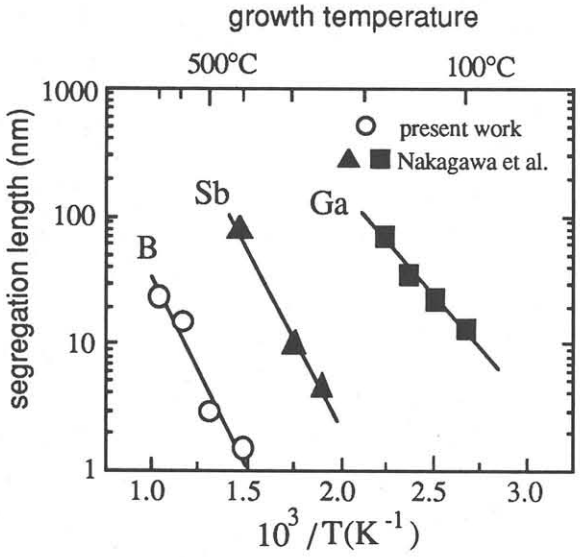

Fig. 5. Arrhenius plots of segregation length of dopant.

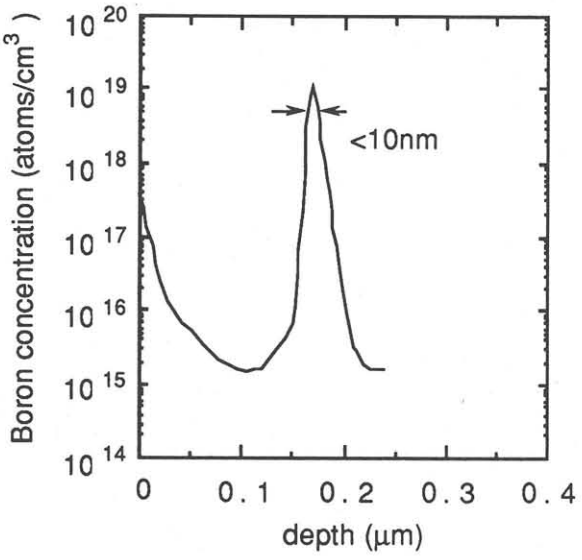

Fig. 6. SIMS depth profile of B in MBE-grown Si (growth temperature = 500 °C).

that of Sb or Ga. As seen in Fig. 6, the growth temperature of 500 °C is effective for atomic-layer doping.

4. CONCLUSIONS

Solid source HBO_2 was shown to have a larger adsorption ratio for a Si surface than for a thin SiO_2 surface formed by wet chemical treatment. A selective adsorption ratio of 43 was observed in HBO_2 adsorption at the substrate temperature of 700°C.

In conclusion, selective B atomic-layer doping using a thin oxide mask was demonstrated for the first time.

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