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Impurity Introduction during Epitaxial Growth of Silicon

In a paper by E. S. Wajda, B. W. Kippenhan and W. H. White,[1] a process has been described which establishes the feasibility of epitaxially growing silicon layers on silicon substrates by the disproportionation of silicon diiodide. This work has been extended in order to investigate the possibilities of codeposition of desired impurities and silicon.

Experimental procedure

The experimental procedure applied was identical with that of Wajda et al, except for the addition of an impurity element. The introduction of an impurity into the reaction tube was done in two different ways: (1) The source zone of the reaction tube was loaded with high-purity silicon and a small weighed quantity of the desired impurity element. (2) Silicon master alloys with known impurity concentrations were used as impurity sources. Pressure and temperature conditions were the same in all runs. The impurities were Group III and Group V elements.

The experiments were evaluated by comparing the impurity concentrations in the source materials with those in the deposits. In those cases where the impurity had been a free element, the total number of impurity atoms put into the source zone divided by the reaction tube volume has been chosen as the significant parameter. The impurity concentration of the master alloys had been specified by the commercial supplier of the material. In one case, the specified concentration had to be corrected, as a result of Hall measurements on the master alloy. The deposited silicon was analyzed by 4-point-probe measurements after lapping off the substrate; concentrations were derived from the resistivities and literature data of carrier mobilities.[2-4] In addition, Hall measurements were made on some of the deposits; agreement of results of both types of measurements was very satisfactory.

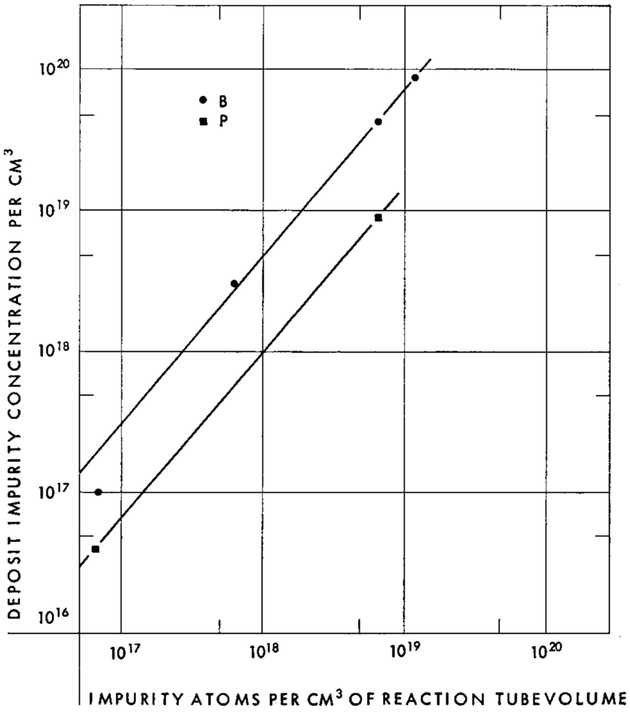
Results

Figure 1 shows the results of experiments in which pure silicon and the free impurity element had been used. The deposits contain impurity concentrations which are proportional to the amount of impurity put into the source region. It is difficult, however, to predict quantitatively the ratio in which the two competing processes, namely, silicon transport and impurity transport, will take place. This will depend not only on the amount of impurity present, but also on tube geometry, source location and surface area of the solid reactants.

In Fig. 2, the impurity concentrations of the deposits are plotted vs. the source concentration for those experiments where silicon master alloys have been used. Most of the experimental points are very close to the straight line which indicates a ratio of source-to-deposit concentration of 1. This means that a silicon deposit grown from a doped silicon source has roughly the same impurity concentration as the source material.

In order to extend the range of concentrations to be investigated, several experiments have been made with

Figure 1 **Impurity concentration of deposited silicon vs. number of impurity atoms initially present in the source region as free elements.**



sources consisting of a master alloy and pure silicon in predetermined weight ratios. It was hoped that these mixed sources would act like one uniform alloy, which had been "diluted" corresponding to the weight ratio. Within certain limits, this was found to be true, and experimental points are included in Fig. 2. However, results become rather unpredictable if the diluting ratio is larger than 100:1 and the experiments are directed to yield very lightly doped deposits. In these cases, one has to consider that it is not really the weight ratio but the surface ratio of pure silicon to master alloy, which determines the over-all impurity concentration. In addition, impurity pick-up from the quartz walls and from the "diluting" pure silicon will have effects that can no longer be neglected.

A few silicon deposits were investigated to check uniformity of the impurity distribution. For this purpose, thin layers of the deposit were lapped off, and 4-point-probe resistivity measurements were made on the remaining deposit between individual lapping steps. From these measurements, the sheet conductivity and the concentration of electrically active impurities of the removed layers can be derived.[5] Results showed in all cases that the impurity concentration was constant within a factor of two throughout the entire deposit.

Discussion

At this time, it is not possible to develop a complete theory of impurity transport and codeposition for the silicon iodide disproportionation process. However, certain principles involved in the impurity codeposition can be visualized and may lead to a better understanding.

The first step in the process of growing doped silicon deposits is the reaction of the solid source with gaseous iodine to form the iodides of silicon and of the impurity, which will vaporize immediately. The free energies of formation of the tri-iodides of B, P, As, and Sb in the standard state are all negative and of comparable values.[6] High-temperature data are not available for most of the compounds, but since they are all of the same chemical nature, their free energies will change with temperature in a way similar to each other. Therefore, the free energies of the impurity iodides at temperatures around 1000°C can reasonably be expected to be of the same order of magnitude. In addition, it can be estimated that the free energies are still negative. This means that the impurity iodides will form readily as soon as an impurity atom of the source is exposed at the surface. Therefore, the ratio of impurity to silicon particles in the gas phase of the source region will be the same as it is in the solid source.

The mixture of iodide vapors is then carried over into the substrate region by diffusion and convection. No change of the impurity-to-silicon ratio is to be expected in this step.

The final step is the deposition of the metals from the iodides, caused by the lower substrate temperature, which requires different vapor pressures. Here the gaseous SiI_2 can be considered as a reducing agent. If a SiI_2 molecule meets another SiI_2 particle at the substrate surface, a silicon atom is added to the lattice, whereas reaction between SiI_2 and impurity iodide particles leads to the incorporation of an impurity atom into the deposit. The experimental results presented in Fig. 2 indicate that both processes, deposition of silicon and of impurities, take place in such a way that the initial source-impurity concentration is being maintained in the deposit. The alternative whether a SiI_2 molecule will react with another SiI_2 or with an impurity iodide particle is therefore determined statistically by the ratio of different particles available in the vapor phase, and none of the two processes seems to be preferred energetically.

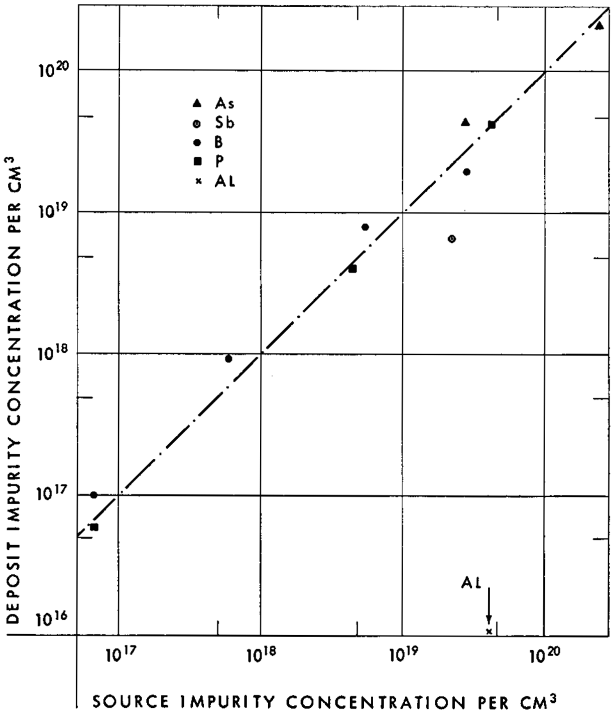


Figure 2 **Impurity concentration of deposited silicon vs. impurity concentration of master alloys used as a source.**

The three experimental points representing concentrations smaller than 10^{18} per cc have been obtained from "diluted" master alloy sources.

There is one exception among the group of experiments using master alloy sources, which indicates that the mechanism described in the foregoing paragraph does not always apply. A deposit grown from a silicon source which contained 4.5×10^{19} atoms of aluminum per cc was found to have an acceptor concentration more than 4 orders of magnitude smaller. This can be explained by the following consideration: AlI_3 shows one remarkable difference from the iodides discussed before: The absolute value of its standard free energy of formation is more than twice as large as those of the other iodides;[6] it is also negative, and therefore AlI_3 is a compound much more stable than the former group of iodides. This means that aluminum iodide will form very readily in the source region, but in the deposition zone it will have only a rather small tendency to being reduced again. Collisions between SiI_2 and AlI_3 molecules will still occur in a statistical manner, however, the yield of these collisions in terms of chemical reaction and deposited metal atoms is much lower than it was in the case of the iodides with the smaller energy of formation. Therefore, it is to be expected that the AlI_3 accumulates in the vapor phase during the experiment, and the aluminum concentration in the deposit should gradually increase accordingly.

Conclusion

In this note it has been shown that the silicon iodide disproportionation process for growing epitaxial layers of silicon is also capable of transporting and codepositing desired impurities. Certain Group III and V elements such as B, P, As and Sb, can be introduced controllably into epitaxial layers of silicon during the growth. Impurity concentrations obtained cover 4 orders of magnitude, reaching far into the degenerate region. Therefore the process as described by Wajda et al is a new tool for the fabrication of various silicon semiconductor structures.

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