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Revisiting the site-competition doping of 4H-SiC: cases of N and Al

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Abstract. Because the well-known site-competition and step-controlled epitaxy rules cannot reasonably describe all the incorporation processes of the main impurities (Al and N) into 4H-SiC during epitaxy, the concept of replacement incorporation was proposed and applied to explain the experimental results published so far. In this model, the transient formation of C or Si vacancies at the surface or sub-surface of terraces is proposed to play a key role by destabilizing the impurities sitting on them. In addition to the availability of these vacancies at the surface, desorption was proposed to be a very important limiting process for Al incorporation while only occasionally relevant for N incorporation. The main 4H-SiC epitaxial growth parameters are reviewed and discussed according to the proposed replacement model.

Introduction.

In situ doping during epitaxy is the most commonly used technique for controlling the doping type and level in thin or thick 4H-SiC active layer(s) to be used in power electronic devices. Up to now, the proposed mechanisms of dopant incorporation were trying to combine two well-admitted rules: "site competition" incorporation [1] and "step-controlled epitaxy" [2]. According to the former rule, N and Al dopants incorporate respectively on C and Si atomic sites of 4H-SiC crystals. According to the latter rule, adatoms (and thus dopants) incorporate at the step edges of the growing surface for avoiding 3C polytype formation. This led to the development of "additive" incorporation models in which impurities contribute to crystal growth (see left part of Fig. 1). But some researchers did not observe the expected crystal off-orientation dependence (and thus step edges incorporation proof) for both N and Al incorporation [3, 4]. It thus cannot be stated as a general rule. Alternatively, some authors proposed impurities incorporation on terraces but by suggesting the creation of unrealistic bonding configurations at the surface. As a matter of fact, a general model thoroughly explaining at least the cases of the most important impurities of 4H-SiC, i.e. Al and N, is still to be found. This is the goal of the present paper.

Replacement model.

We propose a model based on the transient formation of atomic vacancies at the 4H-SiC surface, vacancies on which the considered impurities can condensate from the gas phase. Considering the classical $H_2+C_3H_8+SiH_4$ chemical system used in CVD reactors, C vacancies (V_C) can form due to H_2 etching effect while Si vacancies (V_{Si}) can be created by thermal evaporation. In this model, we will assume that N and Al impurities follow the site competition rule.

When non-intentionally doped 4H-SiC layers are grown, these vacancies are regularly filled by new incoming atoms (precursors) of the same elements. But when intentionally doping with N or Al (using respectively N_2 and $Al(CH_3)_3$ (TMAI) precursors), these impurities can directly replace the vaporized atoms by sitting on the freshly created V_C and V_{Si} respectively (see right part of Fig. 1). With this replacement incorporation, one can easily explain the higher incorporation of N and Al on C-face and Si-face respectively. The corresponding atomic vacancies, i.e. V_C on a C-terminated

surface and V_{Si} on a Si-terminated surface, are intuitively favored so that these sites are directly available for Al and N impurities to sit on. For the reverse configurations (N on Si-face and Al on C-face), the vacancies need to form below the surface which reduces their formation probability and thus these incorporations.

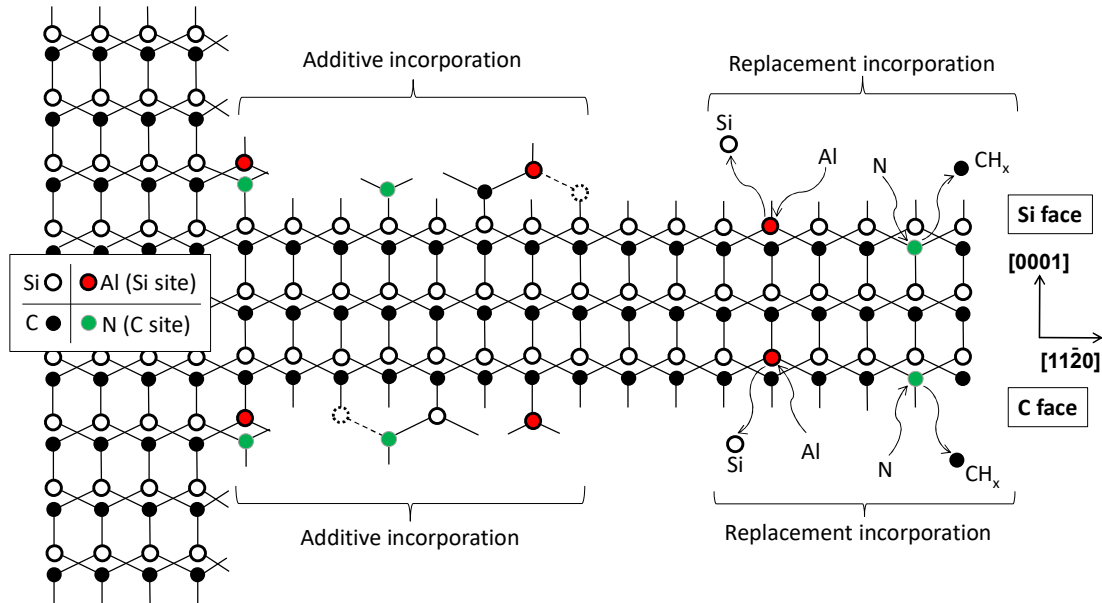


Figure 1. Schematic drawing summarizing the models for N and Al incorporation on both Si and C polar faces of a 4H-SiC crystal: commonly accepted "additive incorporation" and presently proposed "replacement incorporation".

Considering step edges, since the step-controlled homoepitaxy conditions imply preferential atom attachment at these sites, we can reasonably neglect the vacancy-induced Al or N incorporation at the step edges. Dopants can incorporate in an additive manner at these sites and the present model does not exclude this possibility. But due to the surface ratio between step edges and terraces, which is largely in favor of terraces, we believe that the replacement incorporation on terraces shadows the one at step edges.

We will now confront this model to the dopant incorporation trends found in the literature, as a function of 4H-SiC epitaxial growth parameters.

Comparison with experimental results

Effect of temperature. When comparing the reported effect of temperature for both impurities, one can see that they behave differently. $[Al]$ decreases systematically with increasing deposition temperature (independently on polarity) which suggests a desorption-limited incorporation on the entire temperature range (Fig. 2a). In fact, all the parameters investigated here seem to be affected by this high Al desorption which seems to be a constant limitation for Al incorporation during epitaxy independently on the probability of V_{Si} formation at the surface. This does not seem to be the case for N impurity since in most cases $[N]$ is found to increase with temperature (Fig. 2b). According to our model, V_C formation at the surface could be the N incorporation limiting step since this process is obviously thermally activated. Note that on C-face, $[N]$ is less temperature dependent or can even display negative slope with temperature which suggests that N desorption could be also influencing. This is probably due to the fact that V_C formation is very easy on such face so that a N desorption limitation can now be seen. According to this replacement model, the nature of the N-/Al-contributing species is not as important as V_C/V_{Si} availability at the surface.

Effect of C/Si ratio. Concerning the effect of the C/Si ratio, Al and N elements act roughly oppositely (Fig. 3), in accordance with the site competition rule. But again, Al incorporation case looks simpler than N one, especially for polarity effect since [N] can be found higher on Si face than on C face (for low C/Si). According to the proposed replacement model, this has to deal with the occurrence of V_C at the surface. For low C/Si ratios, both polar faces probably have rather similar V_C occurrence probability. Once adsorbed on a V_C , N atom should have a lower desorption probability on the Si-face than on the C-face because of the “buried” configuration on the Si face. In addition, the growth rate is often decreasing at low C/Si ratio so that it also goes towards the increase in N incorporation (see Fig. 6b). These combined effects explain why low C/Si ratio can lead to higher [N] on Si-face than on C-face.

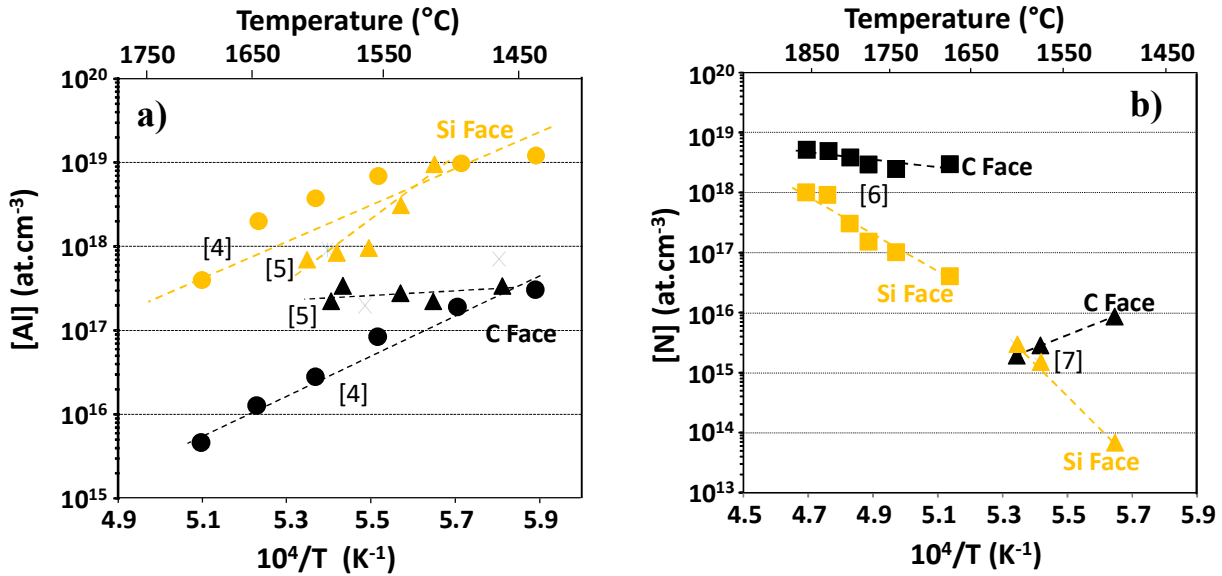


Figure 2. Effect of temperature on the incorporation of a) Al and b) N during 4H-SiC epitaxial growth.

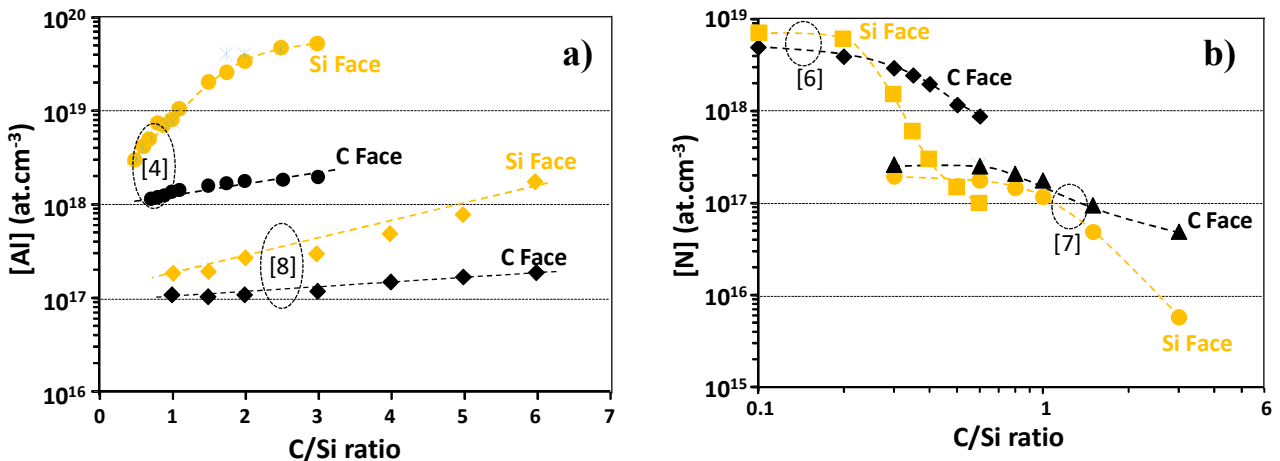


Figure 3. Effect of C/Si ratio on the incorporation of a) Al and b) N during 4H-SiC epitaxial growth.

In the case of Al incorporation, one needs to consider the fact that C/Si ratio change is usually performed at constant Si/Al ratio in the gas phase (constant growth rate fixed by Si flux). This means that the V_{Si} probability of formation is also constant. So, how can [Al] incorporation into 4H-SiC evolve if the V_{Si} availability is constant at the surface? We believe that at high C/Si ratio, the important C coverage should increase Al stability on V_{Si} site of Si face by forming a fourth (and out-of-plane) Al-C bond (see Fig. 4a). This should lead to lower desorption rate and thus higher Al

incorporation. Note that such C coverage is also subjected to constant exchange of carbon atoms with the gas phase and it cannot be seen as the start of 3D nucleation even if it may reduce adatoms diffusion length. Inversely, low C/Si ratio should lead to destabilization of the Al atom sitting on V_{Si} site not only by lack Al-C capping bond but also by V_C formation under the surface (Fig. 4b). This should thus lead to higher desorption rate and thus lower Al incorporation.

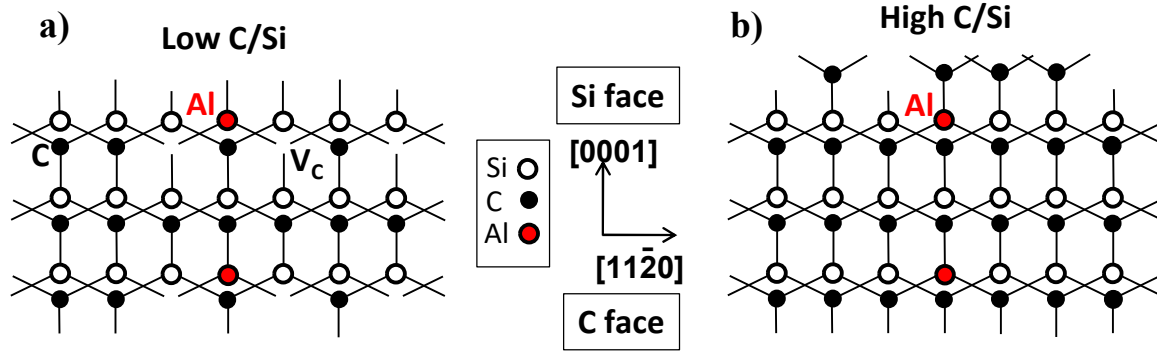


Figure 4. Schematic illustration of the effect of C/Si ratio on Al incorporation during 4H-SiC epitaxial growth according to the discussed replacement model: a) low C/Si ratio and b) high C/Si ratio case.

Effect of pressure. The general effect of growth pressure is very similar for both dopants: their incorporation into 4H-SiC increase regularly with increasing reactor pressure (Fig. 5). This is attributed to the correlative increase of the partial pressure of dopant-containing species with increasing total pressure. When trying to fit these curves with Henry's law ($[D] \propto P_{D_x}^{1/X}$, where X is the number of dopant atoms D in the species responsible for the incorporation), X was found to significantly vary from 0.5 to 1.1 for N (expected $X=2$ for N_2) and from 1.2 to 2.1 for Al (expected $X=1$ for TMAI), see Table 1. It means their respective incorporation is not dependent only on a particular species (for instance the original precursors) so that other parameters have to be taken into account for describing the effect of pressure on dopant incorporation into 4H-SiC. Interestingly, one can see that the slopes are systematically steeper for N incorporation than for Al one. This could be due to the fact that Al incorporation is desorption limited (over the entire pressure range) while N incorporation is V_C formation dependent, process which should increase by increasing H_2 partial pressure.

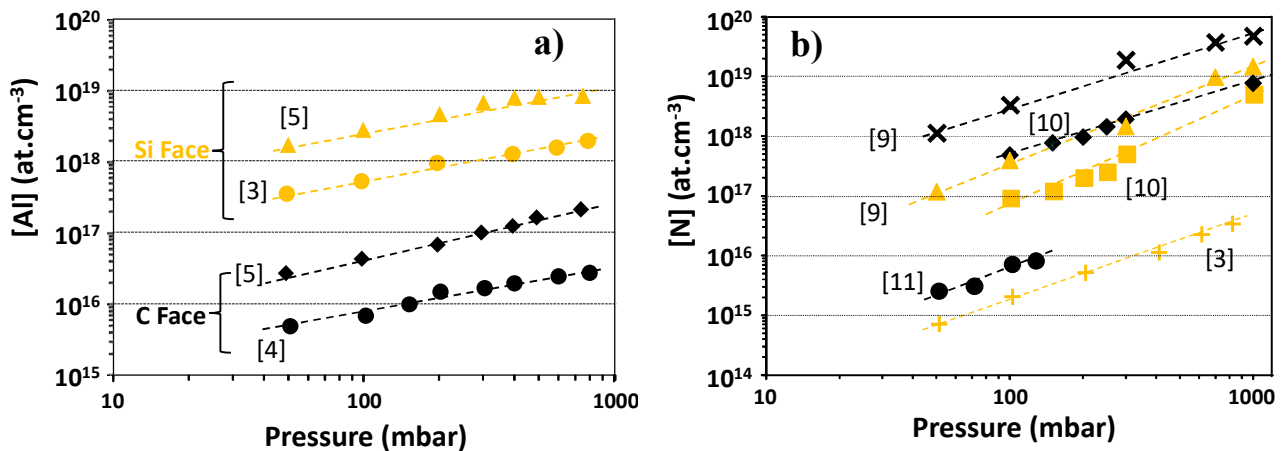


Figure 5. Effect of growth pressure on the incorporation of a) Al and b) N during 4H-SiC epitaxy.

Effect of growth rate. Increasing the growth rate leads to opposite trends for Al and N incorporation into 4H-SiC. For Al, its incorporation systematically increases with growth rate for

both polar faces (Fig. 6a). Considering the high Al desorption rate discussed above, this trend could be related to a decrease of the mean time before adsorbed Al atoms are incorporated into the crystal. This shall lead to lower desorption probability and thus higher Al incorporation at higher growth rate. In the case of N, this trends is only observed for the C-face (Fig. 6b), case for which N desorption limiting incorporation could be effective as previously discussed. For the Si-face, since V_C availability was proposed to be the main limiting factor, one could take into account an increase of the local C/Si ratio when increasing growth rate, as simulated in ref [15,16]. This local increase in C/Si ratio upon increasing growth rate could explain the decrease in N incorporation.

Table 1. Fitting parameter X(Al) extracted from the curves in Fig. 4a, and corresponding growth conditions.

Polarity	Temperature (°C)	X (Al)	Ref
Si face	1600	2.1	[5]
Si face	1650	1.7	[3]
C face	1600	1.2	[5]
C face	1650	1.7	[4]

Table 2. Fitting parameter X(N) extracted from the curves in Fig. 4b, and corresponding growth conditions.

Polarity	Temperature (°C)	X (N)	Ref
Si face	1500	0.67	[9]
Si face	1600	0.5	[10]
Si face	1700	0.68	[3]
C face	1500	0.83	[9]
C face	1600	1.1	[10]
C face	1600	0.72	[11]

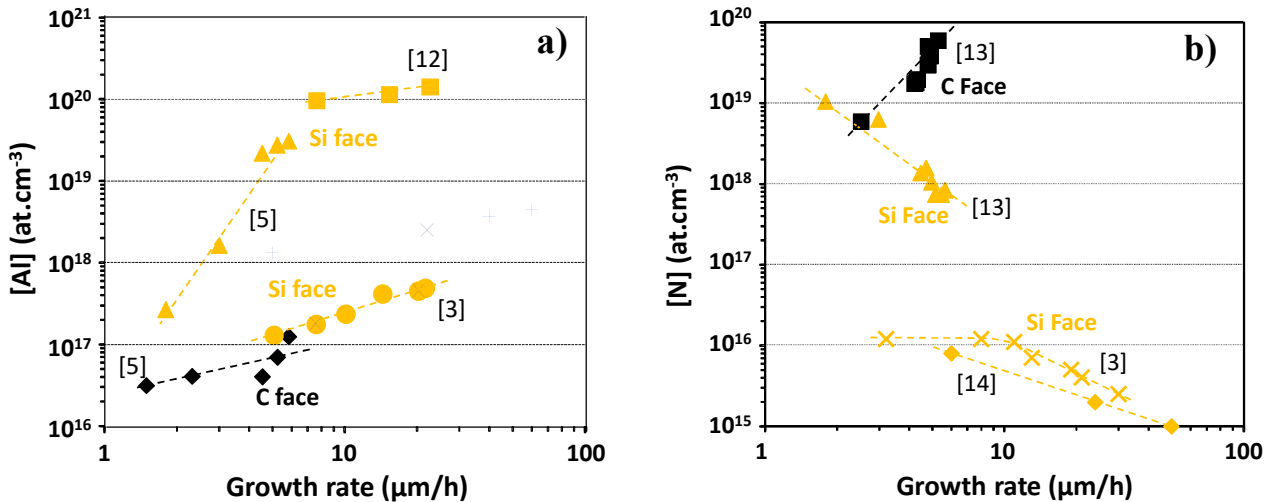


Figure 6. Effect of growth rate on the incorporation of a) Al and b) N during 4H-SiC epitaxy.

Summary

Reviewing the experimental results on both Al and N doping during 4H-SiC epitaxy and applying the replacement incorporation concept to explain these trends allowed highlighting the common points and the differences between both incorporation cases. N incorporation is found very dependent on V_C availability at the terrace surface while Al incorporation is more desorption dependent. Carbon coverage, which fixes the availability of V_C at the terraces, plays also an important role in Al incorporation by reducing Al desorption rate.

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