Supporting Information - 10 pages

Atomic Layer Deposition of Antimony and its Compounds Using Dechlorosilylation Reactions of Tris(triethylsilyl)antimony

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Supporting Discussion

Sb film growth mechanism. *In situ* QMS data of the $SbCl_3$-$(Et_3Si)_3Sb$ ALD process indicated that the fraction of the byproduct Et_3SiCl released during the $SbCl_3$ pulse decreases slightly from (83±5)% to (70±4)% during a measurement session. A similar trend was also observed in the QCM data. The changed mechanism could be restored to the original one with 1) reloading the reactor, 2) cooling and reheating the reactor without reloading it and 3) taking a five hours break without cooling the reactor. The fact that no trend was observed with the $SbCl_3$-$(Et_3Si)_2Te$ process, that has the same byproduct, constitutes solid evidence for the trend here being a true change in the ALD process and not being an artefact caused by instruments. Also the fact that it only requires a break to restore the original mechanism, rules out reactions in the source boats as causing the trend. Therefore the most presumable explanation for the observed trend is a change in the antimony films: taking their final form could require time of the films and the final form could incorporate more $–SiEt_3$ groups.

The change in the antimony films could be *e.g.* crystallization of the amorphously growing films. In that case the crystalline film should be able to incorporate more $–SiEt_3$ groups and the film would grow directly crystalline on a crystalline film deposited previously. Then with proliferating defects the growth mode would gradually change to amorphous also changing the mechanism. Then during a break the entire film would crystallize, and after the break the mechanism would again correspond to crystalline growth.

An exactly opposite mechanism where an amorphous surface incorporates more $–SiEt_3$ groups is also possible. The film growth would start as amorphous and then change to crystalline after a few cycles which causes a slight change in the mechanism. Actually, this type of film growth where amorphous film growth changes to crystalline at some critical thickness is typical for many ALD processes. If this were the case in the $SbCl_3$-$(Et_3Si)_3Sb$ process, the crystalline Sb film surface should change to amorphous during any of the three actions mentioned above, which were noticed to restore the mechanism to the original one. Oxidation of the Sb surface by residual water or oxygen impurities could be responsible for this effect. *In situ* XRD would be required to determine whether either of the two above hypotheses is true.

Yet another explanation for the observed change in the mechanism could be the slow desorption of physisorbed precursors from the reactor walls during the purge periods. Although long purge periods of 55 s were used it is possible that they were still not long enough to desorb all 100% of the physisorbed precursors from the chamber walls. The amount of physisorbed molecules would then slowly pile up leading to an increased amount of desorption during the other precursor pulses and purges. This would lead to increasing amounts of CVD type reactions when the process continues which could then complicate the mechansim. The pile up of physisorbed molecules applies only to the parts in the reaction chamber where the precursors do not meet, that is, source lines right after the flow barrier area (where precursor valving occurs). Whatever the cause may be, the observed change in the growth mechanism is relatively small and does not imply any serious problems in the process.

Supporting Figures

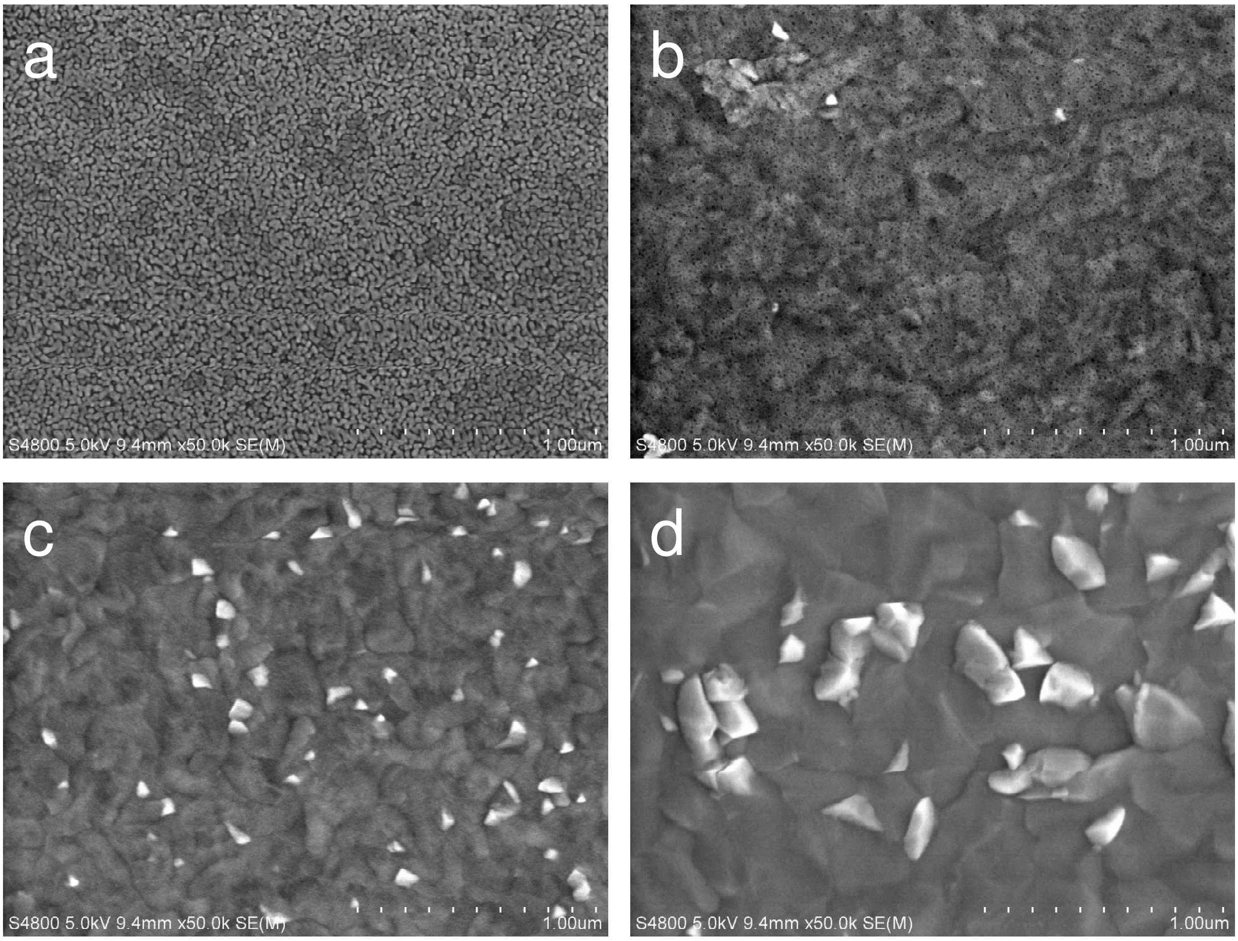

Figure S1. FESEM images of Sb films grown on native SiO_2/Si at 95 °C using (a) 100, (b) 500, (c) 1000 and (d) 2000 ALD cycles.

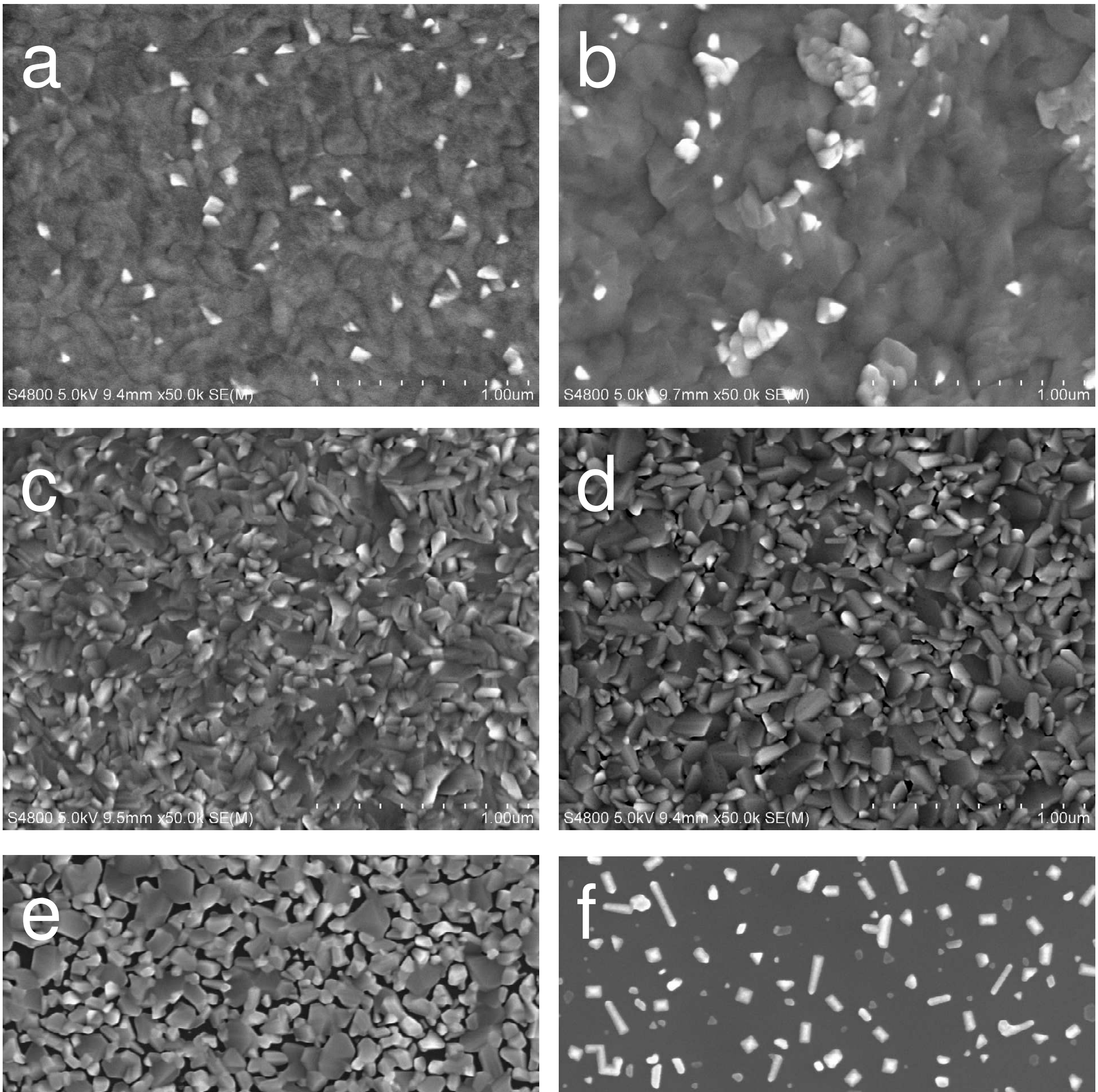

Figure S2. FESEM images of Sb films grown using 1000 ALD cycles at (a) 100 °C, (b) 125 °C, (c) 150 °C, (d) 175 °C, (e) 200 °C and (f) 250 °C.

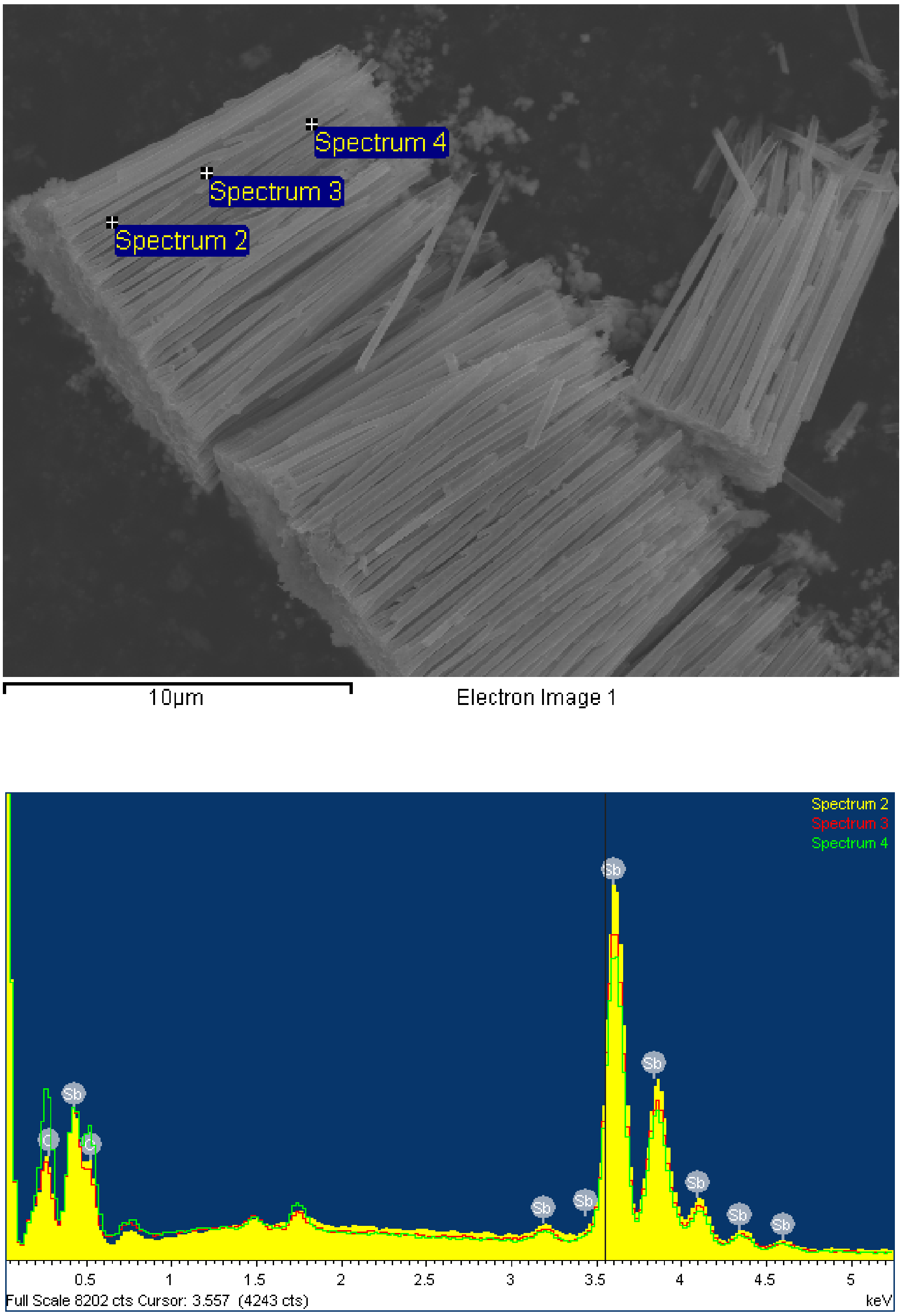

Figure S3. FESEM image and point EDX spectra of Sb nanotubes prepared by template directed ALD.

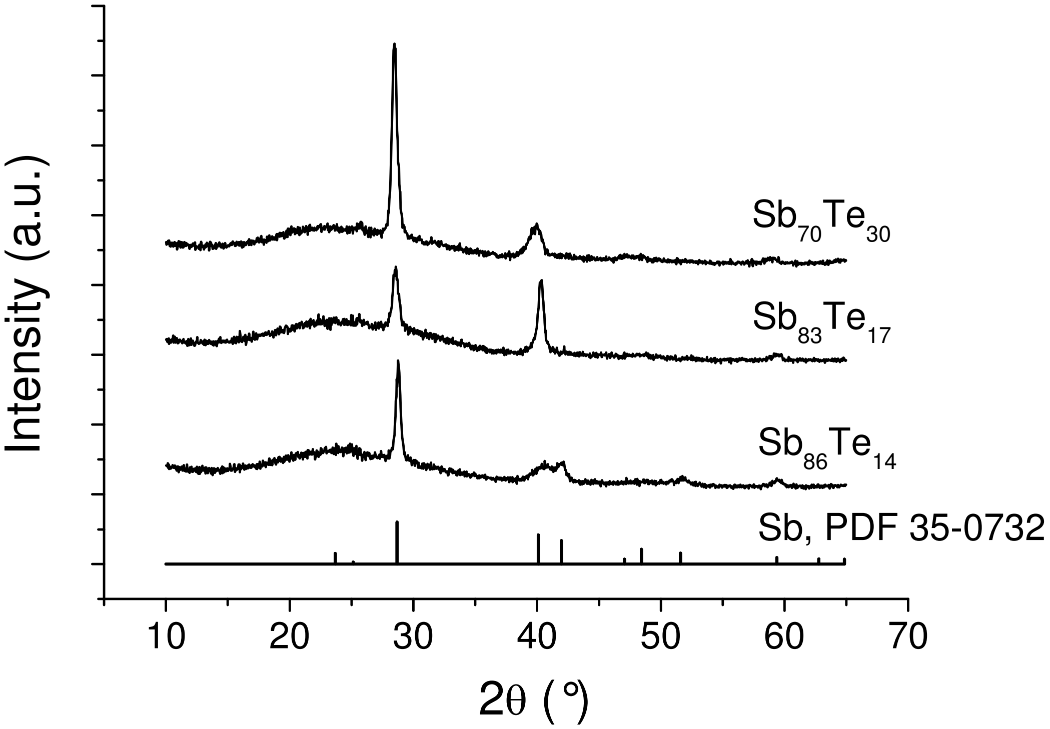

Figure S4. Gracing incidence XRD patterns of Sb-Te films prepared by ALD.

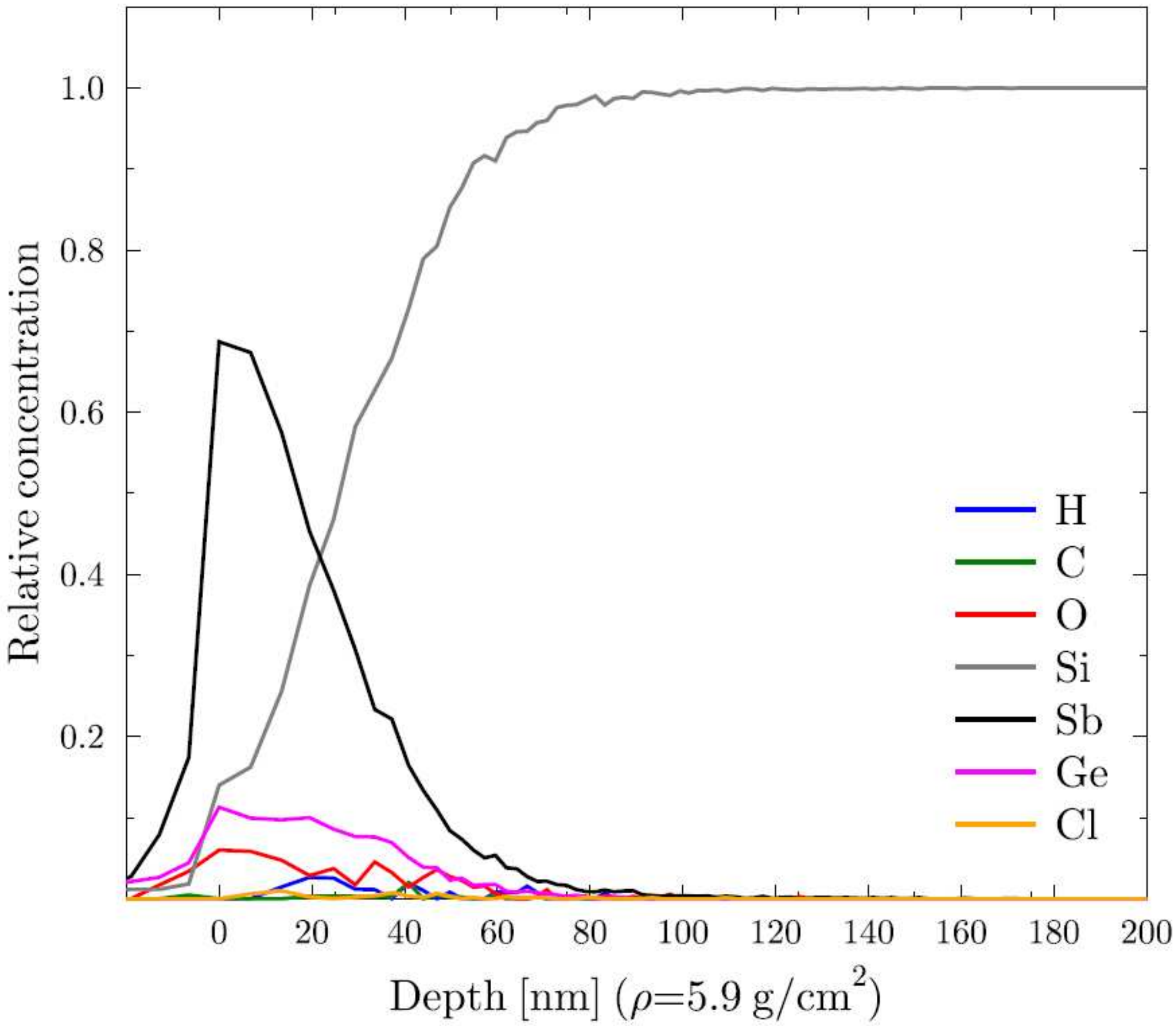

Figure S5. TOF-ERDA depth profile of a $Ge_{22}Sb_{78}$ film grown at 100 °C by ALD.

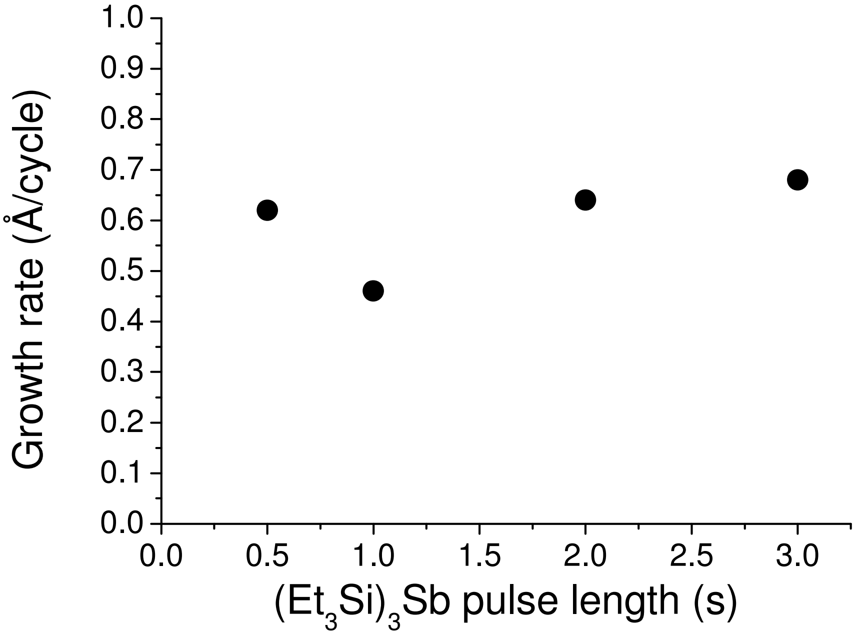

Figure S6. Growth rate as a function of $(Et_3Si)_3Sb$ pulse length of GaSb films deposited at 150 °C.

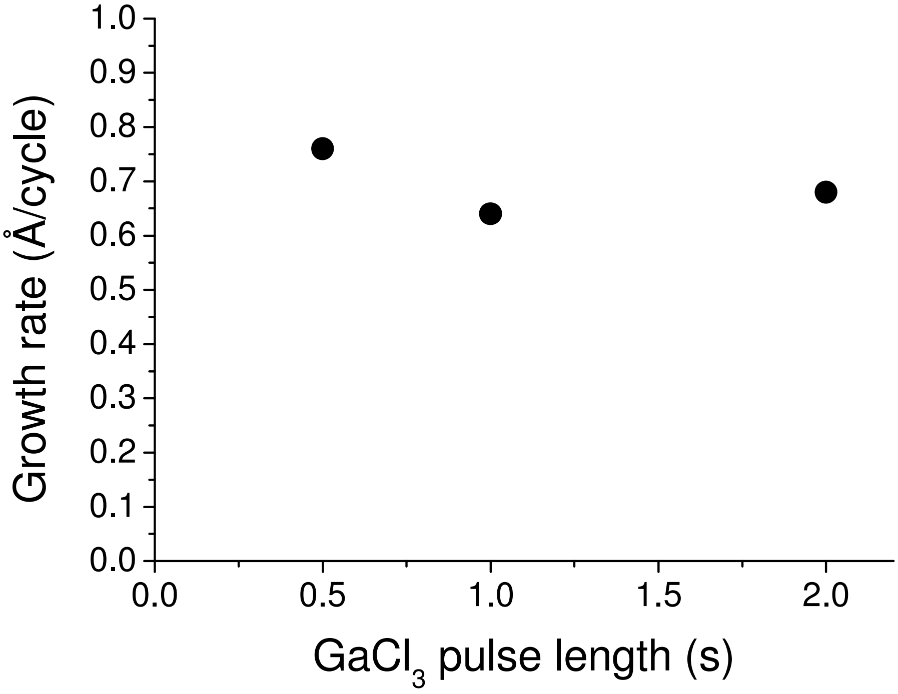

Figure S7. Growth rate as a function of $GaCl_3$ pulse length of GaSb films deposited at 150 °C.

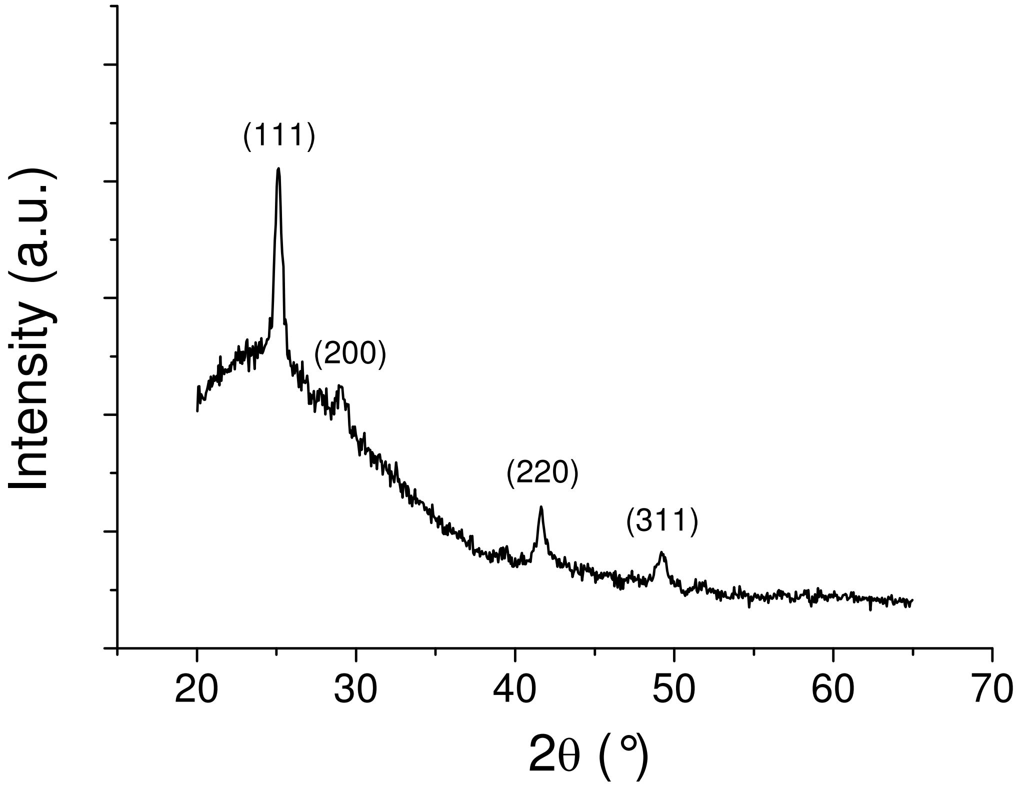

Figure S8. Gracing incidence XRD pattern of an AlSb film prepared by ALD at 300 °C.