

## Atomic Scale Studies of Structure and Bonding in AlPSi<sub>3</sub> Alloys Grown Lattice-matched on Si(001)

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The newly discovered AlPSi<sub>3</sub> alloys<sup>1,2</sup>, which are hybrids of zincblende AlP and diamond cubic Si, may represent a pathway to augmenting the optical performance of elemental silicon as a photovoltaic material, because our preliminary studies suggest that the absorption coefficient of these materials in the visible wavelength range is enhanced relative to Si. Yet, the inherent light absorption might be strongly dependent on the nanoscale structure of the alloy, namely the distribution of the Al-P bonds within the parent Si matrix<sup>3</sup>. Conventional TEM with the JEOL 4000EX and probe-corrected STEM/EELS analyses with Nion UltraSTEM 100 equipped with HERMES<sup>TM</sup> and Gatan Enfinitum<sup>TM</sup> EELS spectrometers were used to study structure and chemistry of Al-P-Si alloys grown nearly lattice-matched on Si (001). Two samples designated 04 and 06 were analyzed in the present work.

Figures 1 (a) and (b) show cross-sectional TEM image of the full epilayer and a diffraction pattern taken along the [110] zone axis. Both the image and diffraction pattern demonstrate the high quality growth of the monocrystalline AlPSi<sub>3</sub> layer grown on Si (001), devoid of threading-type defects or secondary phases within the field of view. Diffraction patterns along the [001] zone axis show no evidence of 200 zincblende spots, except in some isolated regions, indicating that the epilayer has the diamond-like structure. Low magnification EELS scans confirms that both sample 04 and 06 have nearly stoichiometric and chemically uniform AlPSi<sub>3</sub> composition with no sign of phase separation. The monocrystalline character of these samples is corroborated by high-resolution triple-axis XRD analysis of 004, 111 and 224 reflections. For STEM EELS mapping, the probe current and size are carefully balanced between maximizing signal-to-noise (S/N) and minimizing sample damage. Also, ultimate stage stability was required to maintain both high S/N and sufficiently high resolution to resolve the lattice dimers or dumbbells in [110] projection. Atomic-resolution EELS maps obtained from sample 06, presented in Figs. 2 (a)-(e), show that the Al and P atoms preferentially occupy specific sites in the Si matrix, forming Al-P bonds aligned along the growth direction. EELS maps from Sample 04, shown in Figs. 3 (a)-(e), are significantly different from the results of sample 06. There is no sign of preferential Al-P bond alignment with the growth direction. Multiple elemental maps were acquired from different areas of these two samples to confirm the consistency of the EELS results. These STEM EELS results are also complemented with spectroscopic ellipsometry and Raman scattering. The bridge between structural and optical properties is provided by *ab initio* simulations of model crystal systems (Fig.2 (f) and Fig.3 (f)), which are found to be consistent with the STEM EELS results.

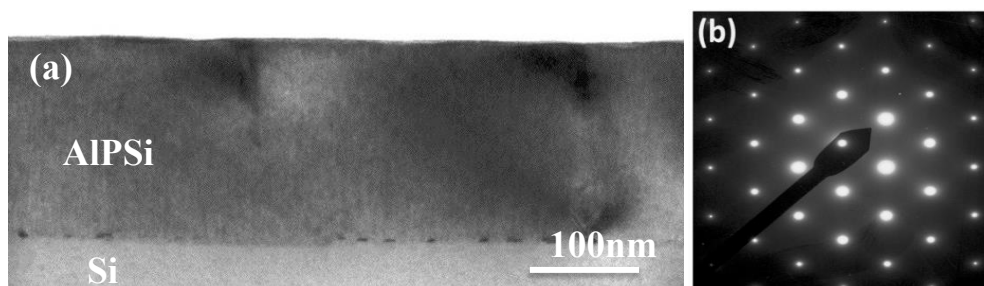
### References:

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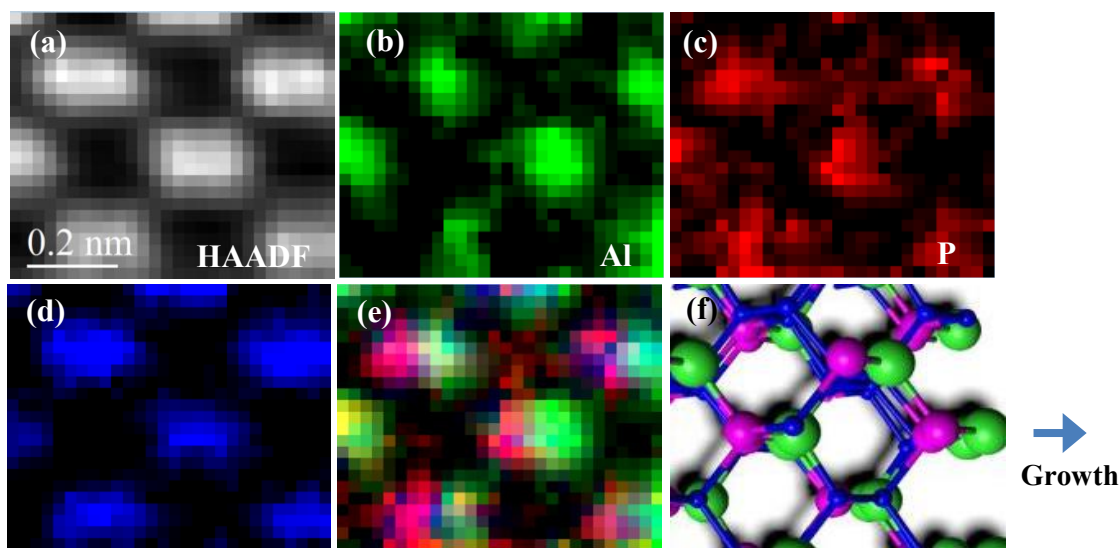
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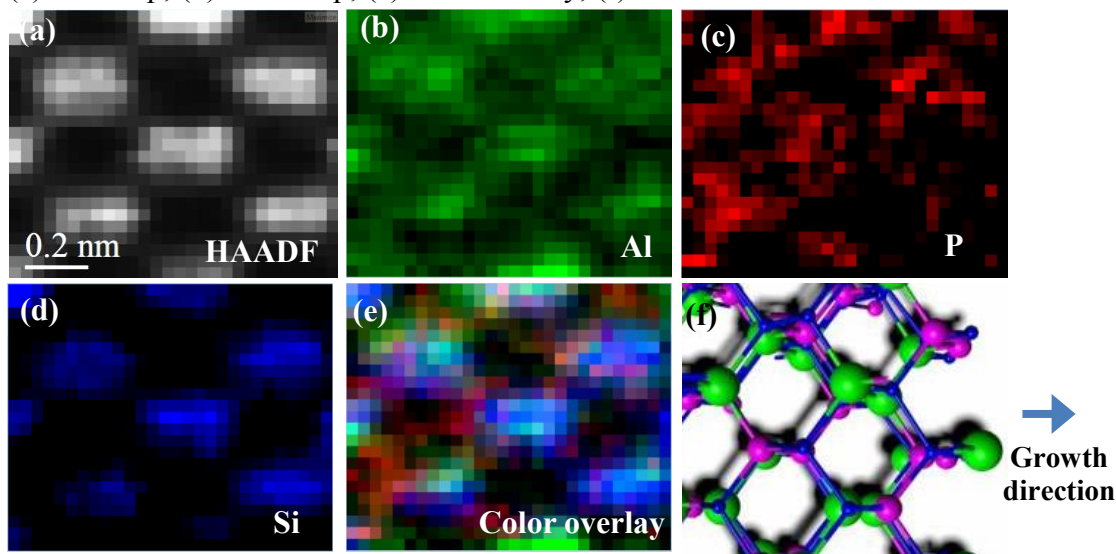
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**Figure 1.** TEM analysis of  $\text{AlPSi}_3/\text{Si}(001)$ ; (a) Cross sectional micrograph of the full epilayer grown lattice-matched on  $\text{Si}(001)$  wafer; panel (b) shows diffraction pattern taken along  $[110]$  zones axis, indicating Si-like symmetry. No evidence of 002 zincblende spots was observed in plan-view images except in isolated regions.



**Figure 2.** MLS fitted STEM EELS map of Al-P-Si alloy (sample 06); (a) HAADF image; (b) Al K map; (c) P K map; (d) Si-K map; (e) color overlay; (f) calculated structure model.



**Figure 3.** MLS fitted STEM EELS map of Al-P-Si alloy (sample 04); (a) HAADF image; (b) Al-K map; (c) P-K map; (d) Si-K map; (e) color overlay; (f) calculated structure model.