AIR LIQUIDE
RESEARCH AND DEVELOPMENT

R&D REPORT

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Author(s): Thomas Laude

TIN PRECURSORS FOR PV

Abstract

Objectives

The goal of this document is to assess the strategical interest for AL to develop a tin precursor for the photovoltaic market. This study is linked to a joint development project proposal received from AIST on c-SiSn deposition.

Results and conclusions

There is a global interest for AL to support the use of a Sn precursor for PV applications, although it is understood that this research is at academic level.

Sn precursors are used to grow c-SiSn alloys, expected with direct band gap (high absorption). They are also used to grow the ternary alloy c-SiGeSn that could allow independent tuning of band gap and lattice constant. Yet, the typical band gap being low (<1.1eV), applications are limited to the red/IR part of the spectra.

Practically, there are technical difficulties for the realization of a device, and in particular the difficulty to grow c-SnSi. The lattice constants of c-Si and c-Sn are very different, and the alloy is only metastable.

Anticipated steps

Based on the present information, we believe that the interest of AL is to pursue the technical follow-up, and to offer a passive support to external R&D efforts, such as the AIST project described here.

Key words

Tin precursor, photovoltaics, solar cell, SiSn

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1. Introduction, solar cell efficiency

There are many ways to lose the solar energy in a solar cell. First of all are "macroscopic" losses which occur before light absorption or after current supply:

Macroscopic losses

"Macroscopic" losses	What can be done
Sun azimuth	Mirrors, motoring
Air diffusion and absorption	Chose site
Reflection	Antireflective coating, dented surface, light trap,…
Thermal radiations from the cell	(passive) cooling
Downstream resistors	Material, load adaptation, increase doping

However, here we are more concerned with "microscopic" losses, which occur either because photon energy is not well converted to electron-hole pairs, or because the pair recombines accidentally before transmitting its energy to the downstream system.

Part of solar light converted to electricity

It has been shown that the best theoretical efficiency that can be expected from a single-homo-junction cell is around 30%.

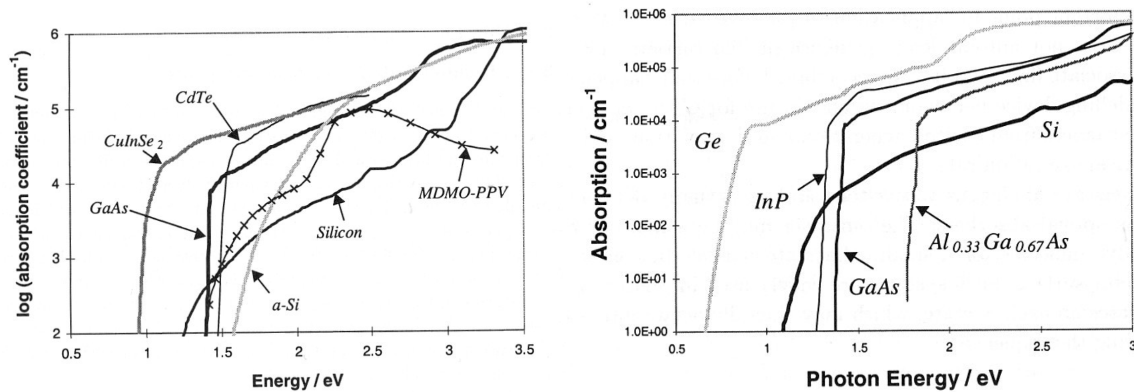
The "microscopic losses	What can be done
Poor absorption: • Low energy photons (below band gap) can not create an electron-hole pair • High energy photons (over band gap) create a pair, but surplus energy is soon lost by intra conduction band transitions (intra-band thermalisation is very fast compared to recombination)	• For a single homo-junction, here is an optimum band gap corresponding to solar light is about 1.4 eV (near GaAs band gap). • One strategy is to use several materials with different band gaps
Early electron-hole recombination: • Recombination within the cell, especially on defects, dopant sites, or grain boundaries. • Recombination after reverse junction current (dark current)	• Use less defective material, mono-crystals in particular • Use thinner layers. • Concentrate the light (multicrossing,…)

Obviously the best PV materials to minimize the losses are:

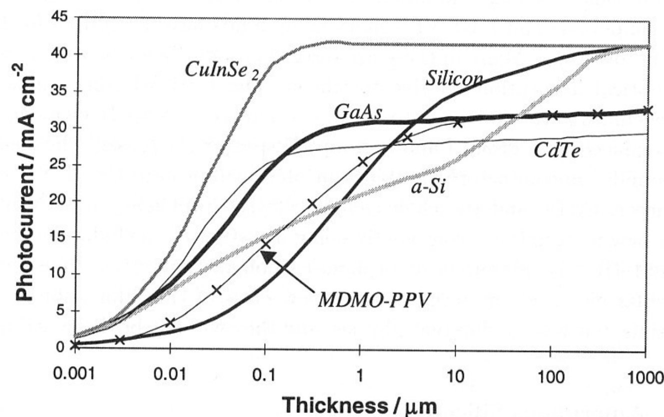
• Crystals (no defects)

• Strong absorbers. In terms, strong absorption enables thin layer design.

In addition, if only one PV material is used, the band gap should be around 1.4eV such as for GaAs, or CdTe.



Absorption of some typical PV materials



Photocurrent versus thickness (used to determine the thickness of the layer)

One very desirable characteristic for a PV material is a direct band gap. The band is direct when valence band and conduction band are on the vertical in the k space.

If the band gap indirect, the creation of an electron-hole pair requires a phonon (photons having no mass, they can not transmit an impulsion to the pair). In terms, the necessity of a phonon in the interaction severely reduces the probability of interaction, and hence reduces absorption.

Direct band gap materials have a sharp rise of absorption just over band gap energy (angular pattern of absorption coeficient). This is the case for GaAs, CdTe, CuInSe2,…

Case of silicon

Crystalline silicon is a typical instance of indirect band gap, with poor absorption over band gap.

Still c-Si is an efficient PV material. This is because the poor absorption is compensated by material thickness (wafer crystal), and hence it is thanks to the very good crystallinity of the material.

On the other hand, amorphous silicon can be considered as a direct band gap material, the material being isotropic. Hence, its absorption is notably higher than that of crystalline Si, and a-Si can be used for relatively thin layers.

Yet a-Si suffers severely of poor crystallinity (recombination associated with defects). Acceptable results of a-Si cells have only been made possible by the passivation of Si dangling bounds with hydrogen (a-Si:H). Still, best a-Si efficiency reported (13%) is only half that of c-Si, and Si-H boundings have low durability under solar exposure. Typically an a-Si:H cell will lose 30% efficiency in the first 6 months of use.

Date	design	% Efficiency
1977	Schottky diode	6
1980	a-Si:H p-i-n	6
1982	a-SiC:H/a-Si:H heterojunction	8
1982	Textured substrates	10
1987	Grading of p-i interface	12
1990	Multigap designs	13

Historical evolution of the performance of a-Si solar cells

2. Effects of alloying Si, Ge and Sn

Si, Ge and Sn are neighbors of the IV group, and therefore their alloys have somehow "blended" properties of the IV group. The goal of alloying is to control the lattice constant. This may be used for two purposes:

1. To accommodate (or strain) a crystal at an interface

2. To change the band gap value or k-space morphology, typically to be closer to a targeted band gap, or to a direct band gap (band gap engineering).

The lattice constant increases from Si to Sn, and the band gap reduces from Si to Sn (metal).

Note: Lattice engineering is also used with alloys of group III-V (InGaAs, InGaAsP, InGaAsSb, AlGaAsSb, InGaAlN). Such alloys are somehow easier to grow as lattice differences are not as severe as for group IV.

Crystalline SiGe

It is the most developed material of the family. It is used in particular as an accommodation layer in semiconductor lasers, waveguide, and p-mos device. It is also studied for its optoelectronic properties in the IR spectrum.

Band gap is between 1.1eV (Si) and 0.65eV (Ge), but with a plateau behavior (see figure) around 0.9eV. The band gap is indirect.

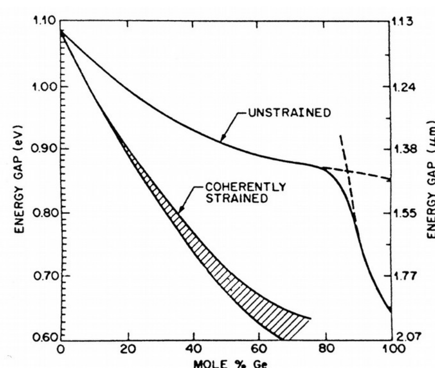


Fig. 5 Fundamental bandgap of Si-Ge pseudorandom alloys as a function of alloy concentration. (Reproduced from People, *et al* [33] with permission of the author.)

Crystalline GeSn

Crystalline GeSn is under study for its direct band gap at 0.5 eV, near Sn 10% (see figure). It is interesting that a direct band gap material can be deposited on Si. Yet this band gap is low (0.5eV) for PV applications.

This could have applications for IR optical devices: heterodiodes, lasers, photodetectors, emitters, modulators, and eventually photovoltaic.

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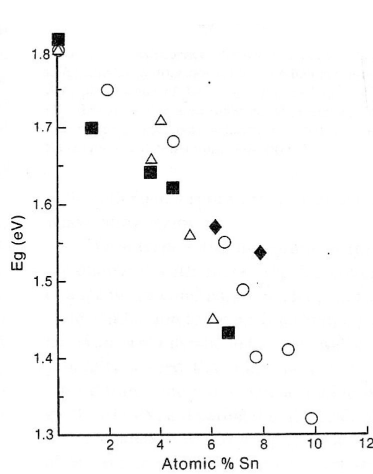
GeSn alloy: A indirect to direct band gap transition is measured near Sn 10% (theoretical calculations give 20%).

Amorphous SiSn

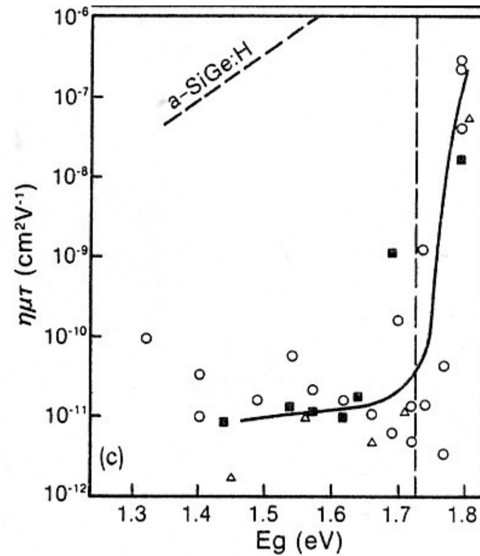
Amorphous SiSn (as well as amorphous SiGe) has been studied for the enhancement of a-Si:H solar cell (in multi-layer design).

Alloying with Sn enables much faster band gap reduction than alloying with Ge. a-SiSn reaches (average band gap) 1.4eV with 10% Sn addition, when a-SiGe alloy requires Ge 50%.

Unfortunately, alloying has been shown to drastically reduce photo-efficiency, as shown below.



Dependence of *a*-SiSn:H band gap (E_g) on Sn content (at. %) as measured by ^{119}Sn Mössbauer spectroscopy. The symbols denote 2.5 W(△), 5 W(○), and 7.5 W(■) rf power levels. Two electron microprobe results (◆) are included for comparison.



Reduction of the band gap for a-SiSn alloy and corresponding degradation of the photoresponse at 600nm (Mahan 1983):

The loss a photo-conductivity has been too drastic for the material to be used in PV applications. For instance, a PV cell with an efficiency of only 2.2% (p-i-n junction) has been reported (Kuwano).

There are two probable (and fundamental) reasons for the degradation of the photoconductivity:

1. Added Sn atoms are poorly bounded to Si. They are interstitial rather than Si substitute. This is probably because the SiSn alloy is not stable thermodynamically.

2. It has been shown that hydrogen preferentially attach to Si, rather than to Sn or Ge. As a result dangling bounds on Sn or Ge cannot be passivated.

Crystalline SiSn

Crystalline SiSn is very difficult to grow. The few reports existing are growth under strain from the buffer layer. For instance, Al-Sameen et al. reported the growth of c-SiSn with Sn4%, and for 150nm thickness. The buffer layer was c-Si(100).

There is not yet a consensus on an eventual direct band gap in c-SiSn. Kouvetakis (2007) expects a direct band gap at Sn 25% based on theoretical considerations. However Al

Sameen, also after theoretical considerations, expects a direct band gap at Sn90-100%, hence near 0.08eV band gap (not useful for PV applications).

Crystalline SiGeSn

There is at least one report of a crystalline SiGeSn growth. Growth was obtained on a GeSn buffer layer (Kouvetakis).

It is hoped that using a ternary alloy enables to chose both band gap and lattice constant separately (in a binary alloy band gap and lattice constant are correlated). This is essential to grow the crystal at given band gap on any specific substrate layer.

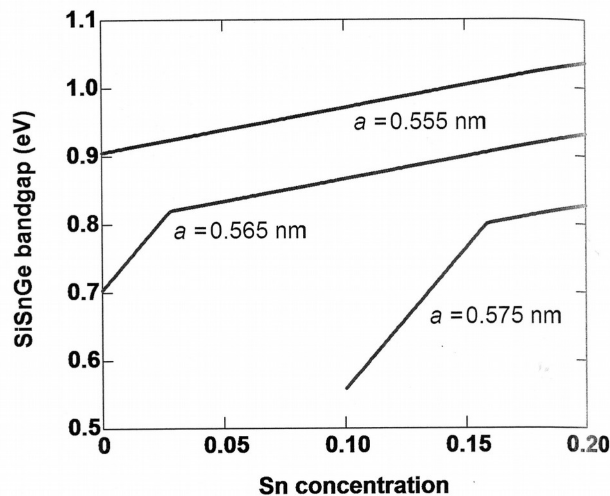


Figure 24 Families of bandgaps versus Sn content for GeSiSn. The Sn and Si contents are adjusted so that the lattice parameter remains constant.

Bandap versus SiGeSn composition (From top to bottom, Si/Ge ratio is 1/1, 1/2, and 1/3)

On the difficulty of growing the Si-Ge-Sn alloys

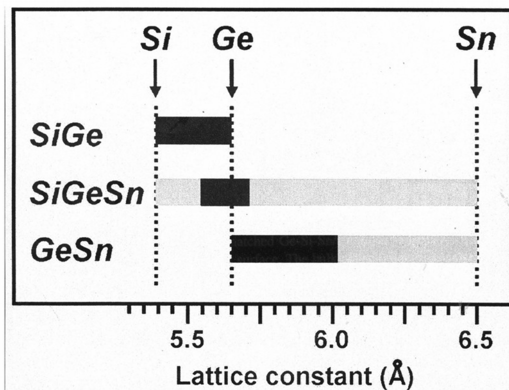


Figure 26 The range of lattice constants achievable in different binary or ternary alloys of Si, Ge, and Sn (*red bars*) and the composition of alloys grown in recent studies (*green bars*).

Lattice constant, and crystal actually grown (Kouvetakis)

Growing an alloyed crystal is made difficult when lattice difference is not too large between the components. This is the case in particular for SiSn and GeSn. It is also more difficult to grow the crystal when the amount of Sn increases.

As shown on figure (Kouvetakis) it was possible to grow:

- c-SiGe alloys, with lattice between 4.4 to 5.65A
- c-GeSn up to Sn 20%, with lattice between 5.65 to 6.02A. GeSn was grown on Si (Kouvetakis) but the strain was released at Si/GeSn interface by dislocations.
- c-SiGeSn (Ge72% Si20% and Sn8%), with lattice: 5.55 to 5.73A. This was grown on a GeSn buffer layer.

c-SiSn has proven more challenging. It was possible to grow c-SiSn with only 4% Sn, for 150nm thickness, and under strain (from Si substrate)

On the other hand, it was possible to alloy SiSn in the amorphous state, up to solubility limit where the phases separate. Amorphous SiSn could be

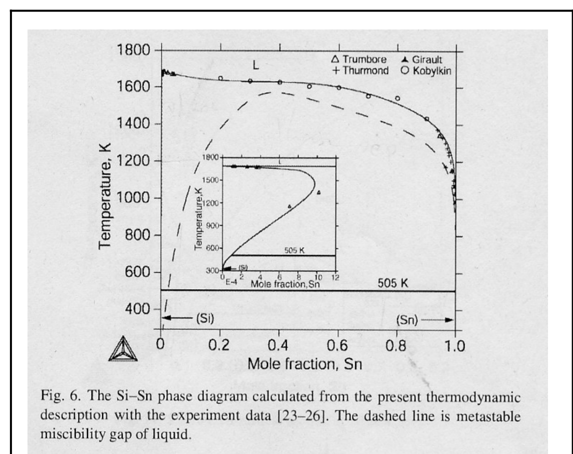


Fig. 6. The Si–Sn phase diagram calculated from the present thermodynamic description with the experiment data [23–26]. The dashed line is metastable miscibility gap of liquid.

Calculated phase diagram shows that Sn is thermodynamically immiscible in Si under equilibrium conditions. (Meng 2006)

made up to Sn 30%. However a-SiSn is metastable and can only be produced in out of equilibrium conditions.

3. TIN PRECURSORS AND DEPOSITION CHALLENGES

Deposition methods

Tin can be deposited by a variety of methods, PVD methods (Molecular beam epitaxy, Sputtering,…) or CVD methods (Ultra High Vacuum-CVD, Glow discharge CVD,..)

Crystalline deposition is difficult both because of the thermodynamic instability of the alloys, and because of lattice accommodation on the growing interface.

State of the art:

- c-GeSn 20%Sn was grown by CVD on Si. Precursor: SnD4+20%H2 (Kouvetakis)
- c-SiGeSn was grown with UVH-CVD with SnD and Si-Ge organics (SiH3GeH3, (GeH3)2SiH2, (GeH3)3SiH) (Kouvetakis)
- c-SiSn was grown by MBE (Al-Sameen Sn 4%,150nm thickness)
- a-SiSn alloy were optained up to Sn 50%, by several out of equilibrium. methods:

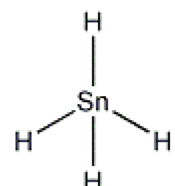
    1. Glow discharge decomposition of SiH4, SnCl4, H2 or SiH4, Sn(CH3)4, H2 (Mahan)
    2. Ion beam assisted deposition: SiH2 ionised, and Sn as vapors
    3. Co-evaporation of Si and Sn
    4. Sputtering Sn in SiH4, Ar atmosphere
    5. Sputtering Si and Sn targets

SnH4 or SnD4 being difficult to handle, physical deposition has usually been preferred.

Tin gas precursors

Hydride

Hydrides have the advantage of bringing no impurity to the deposition. However SnH4 (Stannane) and SnD4 are unstable near room temperature, SnD4 being somehow more stable.

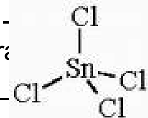


Best stability is reported by mixing SnD4 with H2 20% (reported stable at 22C for several months).

Tin hydride :
Molecular weight: 122.76 g/mol
Aspect: colorless gas
Melting point: -146 C
Boiling point: -52 C
Vapor pressure: 17.5 Torr at -
Decomposes at room tempera
Toxic

Chlorides

SnCl4 is a stable liquid precursor with good volatility. However exhausted chlorine usually has undesirable side effects in the deposition.



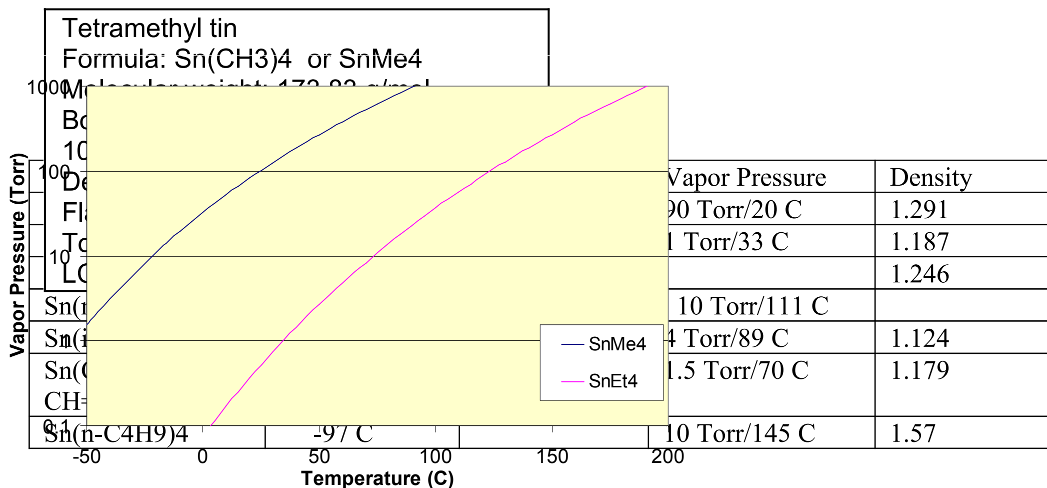
Tin tetrachloride
Molecular weight: 260.50 g/mol
Aspect: orange liquid
Melting point: -33 C
Boiling point: 114 C

Tetraalkyls

Tetraalkyls tin precursors offer higher deposition temperature, and therefore may allow better ordering of the amorphous alloy. However such compounds are toxic and the problem of carbon contamination exist.

Tetraethyl tin
Formula: Sn(CH2CH3)4 or SnEt2
Molecular weight: 234.94 g/mol
Boiling point= 180 C
1 Torr at 33 C, 2 Torr at 48 C
Density= 1.187
Flash point= 53 C
Highly toxic: LD50(oral, rat)= 9 mg/kg

Tetramethyl tin
Formula: Sn(CH3)4 or SnMe4



			Vapor Pressure	Density
			90 Torr/20 C	1.291
			1 Torr/33 C	1.187
				1.246
Sn(			10 Torr/111 C	
Sn(			4 Torr/89 C	1.124
Sn(CH=			1.5 Torr/70 C	1.179
Sn(n-C4H9)4	-97 C		10 Torr/145 C	1.57

4. NEDO/AIST PROJECT ON SI-SN

End 2008, NEDO/AIST is launching a project to make a thin film 3-layer cell with target of 40% efficiency. (Prof. Kondo/AIST Tsukuba)

One part of this project aims at building a bottom layer c-SiSn (project of Dr. Nagai) to provide absorption in the 0.8-1.1eV range. AL has been proposed to participate in this, as a joint development project.

Meanwhile, 4 others techniques are also tested (by different AIST group) for the bottom layer: 2 types of SiGe layers, a crystalline Ge layer, and an organic layer.

Dr Nagai targets for the SiSn layer are:

- Sn 30% with direct band gap (Note: This is very high to grown a crystal. And the existence of a direct band gap is still under question.)
- monocrystal or polycrystal
- Thickness around 300nm
- Substrate of c-Ge at start, and possiblly GeSn in the mid-term. (accommodation issue probable)

Main reference cited => J. Kouvetakis and V. Chizmeshya, J. Mater. Chem. 2007, 1649-1655

The deposition technique is proposed as follow:

- Sn deposition by thermal CVD, or plasma CVD.
- Candidate precursors: SnCl4, SnH4 and Sn(CH3)4. (ALL suggested starting with SnCl4 for practical reasons.)
- Low temperature deposition to avoid Si and Sn segregation.

AIST requested to ALL:

- Sn precursor supply
- Sn precursor handling know-how
- Supply line and exhaust line know-how
- Related maintenance.

Known difficulties:

- Crystalline Si-Sn is notably difficult to grow as it is not stable thermodynamically. Growth under interfacial strain may be successful.
- SnH4 is unstable

Strategic perspectives for AL

Market assessment is not meaningful today. It is understood that this is an academic project.

Yet there is a global interest for AL to support the use of Sn gaseous precursors in PV and electronics, the actual uses of Sn precursors being open in the future.

The cost of adding Sn to a cell is high, but not fatal, compared to the present price of an a-Si cell (130eur/m2)

Assuming,

- SnH_4 cost at 1150 eur/mol (Estimation by Tarutani-san/ALL)
- A c-SiSn layer of 1 micron with Sn 10%

we estimate Sn costs around 10 eur /m².

5. CONCLUSIONS

There is a global interest for AL to support the use of Sn precursors for PV application, although it is understood that this research is at academic level, and that there is no guaranty of a marketable product.

Sn precursors could be used either to form c-SiSn alloys, or to form the ternary alloy c-SiGeSn, that allows independent tuning of band gap and lattice constant. Yet the band being low (<1.1eV) this more for red/IR part of the spectra.

However, we have also seen that there is a fundamental difficulty in growing a crystal containing Sn. The reason is the large lattice constant, which leads to SiSn and GeSn alloy being only metastable.

Based on the present information, we believe that the interest of AL is to pursue the technical follow-up, and to offer a passive support to external R&D efforts, such as the AIST project described here.

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