

Solvents for liquid phase epitaxial growth of silicon thin film for photovoltaics based on calculation

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태양전지용 액상에피텍시얼 실리콘 박막성장을 위한 용매에 관한 계산

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Abstract The proper choice of the solvent is a prerequisite for solution growth of silicon. In the present work, the temperature to dissolve at least 1 atomic% silicon was calculated in various molten solvents.

요약 실리콘의 용액성장을 위해서는 우선 적절한 용매의 선택이 선행되어야 한다. 이 논문에서는 최소한의 실리콘(1 atomic%) 고용할 수 있는 온도를 여러 용매를 대상으로 계산하였다.

1. Introduction

Liquid phase epitaxial growth (LPE) has

been widely used for growing group III-V semiconductor films. Recently, this technique was employed to grow epitaxial silicon. Basi-

cally, this method results in the direct precipitation of the solute on the substrate from an molten saturated solution. The crystallographic orientation of the epitaxial layer is determined by that of the substrate. In this method, a substrate which generally of the same composition as the solute, is heated to a temperature approximately equal to that of the solution and then brought into contact with the solution. Usually the solution is in a saturated state. The temperature is normally raised 5 ~ 10°C to etch back a portion of the substrate surface to remove mechanical damage, to provide good wetting, and to produce a flat junction. Next, the temperature is lowered in a controlled manner and crystal growth occurs on the substrate. Epitaxial layer growth can be halted by separating the substrate and solution after an predetermined period of time. Crystal growth will, of course, cease automatically when the temperature is lowered far enough that the solute solubility approaches zero. After the growth time, the substrate is separated from the solution. It is necessary to ensure that the surface is free from any drops of excess solution.

2. Phase relationships

In order to understand the solution growth process solid-liquid phase diagrams must be considered. The temperature-composition equilibrium phase diagram of Fig. 1 illustrates the phase relationship for a binary or pseudo-binary system which is typical of

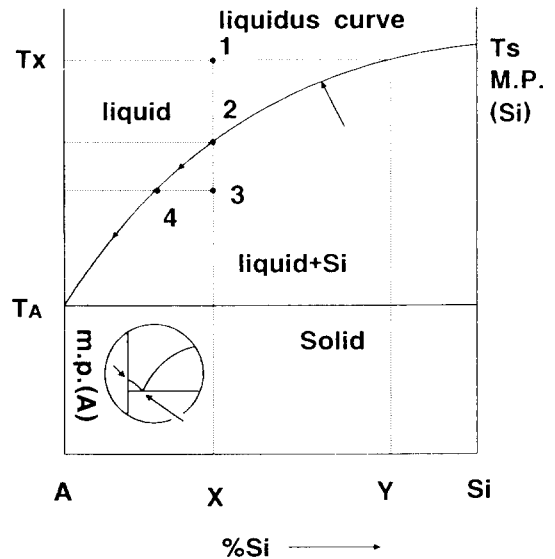


Fig. 1. Schematic temperature-composition phase diagram for the system metal A-Si.

that required for solution growth of Si. T_A is the melting temperature of the metal solvent, A, and T_S is the melting temperature of the silicon. Component A may be a single element or a eutectic alloy. The curve from T_S to T_A in Fig. 1 is called the liquidus curve, which shows the maximum solubility of silicon in a molten alloy. Thurmond and Kowalchik [1] show that a good approximation to these curves for silicon is

$$T = \frac{\Delta H_{Si}^F + a(1-x)^2}{\Delta S_{Si}^F - R \ln x + b(1-x)^2} \quad (1)$$

where T is the temperature (K), x is the atom fraction of silicon in the saturated liquid, ΔH_{Si}^F and ΔS_{Si}^F are the enthalpy and entropy of fusion of silicon (12082 cal/g-atom and 7.170 cal/g-atom K : Avogadro's number times Boltzmann's constant), and a and b are parameters dependent on the

metal in which the silicon is dissolved, (related to partial molar enthalpies and excess entropies respectively).

Thurmond and Kowalchik extract a and b from experimental solubility measurements of silicon in a number of molten metals (Ag, Al, As, Bi, Cu, Ga, In, Pb, Sb, Sn, Tl, Zn).

Lehoc and Slobodskoy [2] address the problem (in a fairly rudimentary way) of calculating the solubility in a binary metal molten alloy, knowing the solubility in each of the constituents. (They make a first order approximation as to how the molar excess free energy of the ternary alloy might be described). The result of their analysis can be expressed in the following way. Equation (1) still describes the liquidus, but with a and b given by :

$$a = (a_{12} + a_{13}r - a_{23}r/(1+r))/(1+r) \quad (2)$$

$$b = (b_{12} + b_{13}r - b_{23}r/(1+r))/(1+r) \quad (3)$$

where component 1 is silicon and components 2 and 3 are the metals constituting the binary melt. a_{12} , b_{12} , a_{13} , b_{13} are the parameters as determined by Thurmond and Kowalchik. a_{23} and b_{23} are the corresponding parameters for the binary metal system (no silicon!), assuming this system can be described by such parameters (a quasi-regular solution model). r is the ratio x_3/x_2 in the ternary system.

The binary alloy calculations (Table 1) were based on Thurmond and Kowalchik's data plus their values of ΔH_{si}^F , ΔS_{si}^F and R (12100, 7.189 and 2 respectively). Values of

a_{23} and b_{23} were estimated from the partial molar enthalpies of the binary system involved [3]. Thurmond's data is suspect for some metals, notably gold!

In Fig. 1 a solution of composition X at temperature T_x is represented by position 1 in the completely liquid region of the diagram. Since position q lies above the liquidus, solid-liquidus equilibrium can be attained by movement to the liquidus line. This can be accomplished either by a change in composition of the solution to correspond to Y, by a reduction in the temperature of the solution to T_c which is represented by position 2 of the liquidus line, or by the use of a combination of both processes.

In any case, after the liquidus is reached, further cooling under equilibrium conditions will cause Si to precipitate. This assumes that no supercooling of the saturated solution occurs as the temperature is lowered. Since the average composition of the entire solid-liquid system must remain constant during the process, the solution becomes richer in A as Si precipitates from it. Thus, the amount of solid Si which is formed at a given temperature is in direct proportion to the distance from pure A to the liquidus line at that temperature. The composition of remaining liquid solution follows the liquidus line towards T_A as indicated by the arrows. It is important to note here that it is the component with the higher melting point which precipitates from the solution under these conditions.

3. Calculated solvents for solution growth

For the solution growth of silicon, metals which do not form compounds with silicon are of most interest in the present case since those that do may lead to silicide rather than pure Si deposition from solution.

These metals, with the exception of Be, are arranged within the Periodic Table in the “extended delta” formation of Table 1. They can be further sub-divided into three groups. Ge is unique in that it is completely miscible with silicon in both the liquid and molten state. These mixtures, however, are nominally molten only above the melting point of Ge (940 °C). The remaining metals can be divided into two categories. Type I metals (Ag, Al, Au, Be) all form a simple eutectic with silicon with the eutectic temperature suppressed more than 80 °C below the melting point of the metal and with more than 10 atomic (at.%) Si at the eutectic point.

Type II metals (Bi, Cd, Ga, Hg, In, Pb,

Table 1
“Extended delta” region in the periodic table showing metals which, together with Be, do not form stable silicides

IB	IIB	IIIA	IVA	VA	VIA
		B	C	N	O
		Al	Si	P	S
Cu	Zn	Ga	Ge	As	Se
Ag	Cd	In	Sn	Sb	Te
Au	Hg	Tl	Pb	Bi	Po

Sb, Sn, Tl, Zn) have lower melting points (630 °C) and form a pseudo-eutectic with the eutectic temperature 1 °C or less than the metal melting point and less than 1 % at. Si at the eutectic point. Schematic binary phase diagrams with silicon of Type I and Type II metals are shown in Fig. 2.

From the point of view of depositing silicon from solution at low temperature, this clear distinction leads to either an over- or under-abundance of riches. None of the Type II metals dissolve enough silicon (> 1 % atomic) at temperatures below 600 °C to be a practical solvent for Si LPE growth at

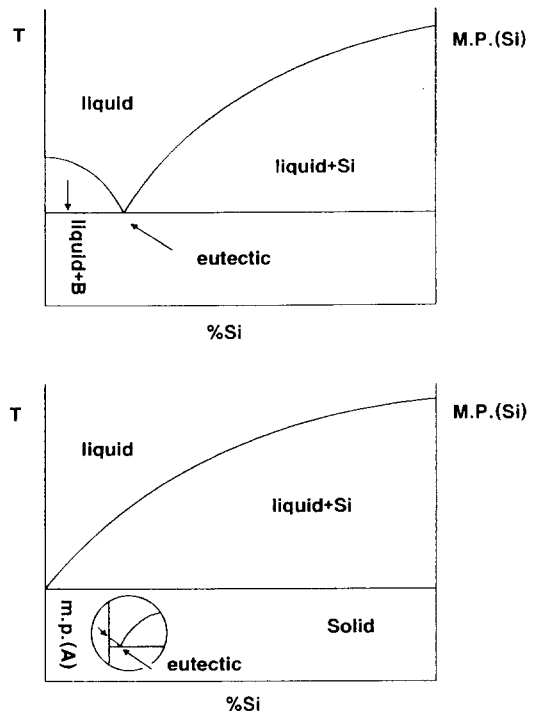


Fig. 2. Schematic binary phase diagrams with silicon of : (a) “Type I” metals (Ag, Al, Au, Be) ; and (b) “Type II” metals (Bi, Cd, Ga, Hg, In, Pb, Sb, Sn, Tl, Zn).

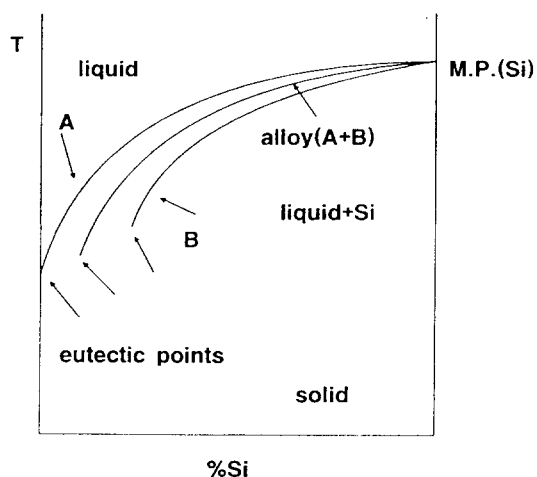


Fig. 3. Pseudo-binary phase diagrams of silicon with alloys of Type I and Type II metals (B and A, respectively, on the above diagram). Increasing the Type II metal content reduces both the temperature and silicon content of the system eutectic.

very low temperature, except gallium. Ga has the highest Si solubility of the Type I metals with LPE demonstrated at temperatures down to 610 °C [4].

On the other hand, the Type I metals, Au and Al require an excess amount of silicon in solution ($> 10\%$ atomic) to remain molten at such temperature. The solubility of Si in both Type I and Type II metals is well known [1], apart from the case of Cd, Hg and Tl where all indications are that the solubility is low.

Of the Type I metals, only Au would permit LPE at temperatures below 500 °C. However, the large Si content ($> 15\%$) required to maintain the molten state at such temperatures may give rise to problems with controlling deposition rates and Si nuclea-

tion within the melt, as previously noted.

A solution to this problem is to consider a metallic alloy as the solvent. In an earlier study, Girault et alii [4] showed increased low temperature silicon solubility using Al/Ga alloys and demonstrated growth from such alloys at temperatures down to 450 °C. The films were, however, too heavily doped with Al and Ga to be of interest for electronic devices.

Using the theory outlined in Section 2, the temperature required to dissolve 1 % silicon was calculated for a range of metal alloys. The results are shown in Table 2. It became apparent from this work that the most promising alloys were those of a Type I and Type II metal. With increasing Type II metal included in the alloy, the eutectic, as shown on quasi-binary diagram of Fig. 3, is displaced to lower temperatures and lower silicon content.

Particularly promising were alloys of Au with Type I metals which appeared capable of giving the required solubility at the lowest temperature.

Table 2

Calculated temperature to dissolve at least 1 % Si in molten alloys

Ag(830 °C)

Ag:	1001 °C (20% Si)
Ag _{0.5} Au _{0.5}	548 °C (20% Si)
Ag _{0.9} Au _{0.1}	929 °C (20% Si)
Ag _{0.6} Bi _{0.4} :	741, 810 °C (liquid to 500 °C)

$\text{Ag}_{0.8}\text{Pb}_{0.2}$:	563 °C (invalid, below liquidus)	<u>Bi(2274 °C)</u>	
$\text{Ag}_{0.5}\text{Sn}_{0.5}$:	612, 671 °C (liquid to 500 °C)	$\text{Bi}_{0.4}\text{Ag}_{0.6}$	741, 810 °C
$\text{Ag}_{0.05}\text{Zn}_{0.95}$:	(liquid to 480 °C)	$\text{Bi}_{0.5}\text{Au}_{0.5}$	526 °C
		$\text{Bi}_{0.8}\text{Au}_{0.2}$	980 °C
		$\text{Bi}_{0.9}\text{Au}_{0.1}$	1085 °C
<u>Al(577 °C)</u>			
$\text{Al}_{0.1}\text{Ga}_{0.9}$:	581 °C (exp. 600 [4])	<u>Cu(802 °C) - silicide</u>	
$\text{Al}_{0.2}\text{Ga}_{0.8}$:	547 °C (exp. 580 [4])	<u>Ga(615 °C)</u>	
$\text{Al}_{0.4}\text{Ga}_{0.6}$:	477 °C (540 °C experimentally [4])	$\text{Ga}_{0.6}\text{Al}_{0.4}$	477 °C (exp. 540 °C [4])
$\text{Al}_{0.09}\text{Sn}_{0.9}$	793 °C (700 °C experimentally [4])	$\text{Ga}_{0.8}\text{Al}_{0.2}$	547 °C (exp. 580 °C [4])
$\text{Al}_{0.1}\text{Sn}_{0.9}$	614 °C (agrees exp. [4])	$\text{Ga}_{0.9}\text{Al}_{0.1}$	581 °C (exp. 600 °C [4])
		$\text{Ga}_{0.0}\text{Zn}_{1.0}$	657 °C
		$\text{Ga}_{0.5}\text{Zn}_{1.5}$	628 °C
<u>Au(370 °C)</u>			
$\text{Au}_{0.1}\text{Ag}_{0.9}$	929 °C (20 % Si)	<u>Ge(957 °C)</u>	
$\text{Au}_{0.5}\text{Ag}_{0.5}$	548 °C (20 % Si)	$\text{Ge}_{0.0}\text{Zn}_{1.0}$	657 °C
$\text{Au}_{0.0}\text{Bi}_{1.0}$	1174 °C	$\text{Ge}_{0.04}\text{Zn}_{0.96}$	643, 650 °C
$\text{Au}_{0.1}\text{Bi}_{0.9}$	1085 °C	$\text{Ge}_{0.15}\text{Zn}_{0.85}$	613, 633 °C
$\text{Au}_{0.2}\text{Bi}_{0.8}$	980 °C		
$\text{Au}_{0.5}\text{Bi}_{0.5}$	526 °C	<u>In-(~850 °C)</u>	
$\text{Au}_{0.0}\text{Sn}_{1.0}$	851 °C	<u>Pb(1237 °C)</u>	
$\text{Au}_{0.1}\text{Sn}_{0.9}$	771, 809 °C	$\text{Pb}_{0.2}\text{Ag}_{0.8}$	563 °C (below liquidus)
$\text{Au}_{0.5}\text{Sn}_{0.5}$	561 °C	$\text{Pb}_{0.2}\text{Sn}_{0.8}$	830 °C (exp. [4])
$\text{Au}_{0.0}\text{Ti}_{1.0}$	1137 °C	$\text{Pb}_{0.84}\text{Sb}_{0.12}\text{Sn}_{0.04}$	~ 1200 °C (exp. [4])
$\text{Au}_{0.2}\text{Ti}_{0.8}$	974 °C	$\text{Pb}_{0.32}\text{Sb}_{0.52}\text{Sn}_{0.16}$	~ 1200 °C (exp. [4])
$\text{Au}_{0.5}\text{Ti}_{0.5}$	561 °C		
$\text{Au}_{0.0}\text{Zn}_{1.0}$	567 °C	<u>Sb(~770 °C)</u>	
$\text{Au}_{0.1}\text{Zn}_{0.9}$	634, 677 °C (liquid at 500 °C)	<u>Sn(851 °C)</u>	
		$\text{Sn}_{0.5}\text{Ag}_{0.5}$	612, 671 °C
<u>Be(1030 °C)</u>		$\text{Sn}_{0.91}\text{Al}_{0.09}$	793 °C (700 °C exp. [4])

$\text{Sn}_{0.5}\text{Au}_{0.5}$	473, 588°C
$\text{Sn}_{0.8}\text{Au}_{0.2}$	717, 785°C
$\text{Sn}_{0.9}\text{Au}_{0.1}$	771, 809°C
$\text{Sn}_{0.8}\text{Pb}_{0.2}$	830°C (exp. [4])

Tl(1137°C)

$\text{Tl}_{0.5}\text{Au}_{0.5}$	561°C
$\text{Tl}_{0.8}\text{Au}_{0.2}$	974°C

Zn(657°C)

$\text{Zn}_{0.95}\text{Ag}_{0.05}$	(liquid at 500°C)
$\text{Zn}_{0.9}\text{Al}_{0.1}$	614°C (agrees exp. [4])
$\text{Zn}_{0.9}\text{Au}_{0.1}$	634, 677°C (Zn > 0.9 liquid)
$\text{Zn}_{0.5}\text{Ga}_{0.5}$	628°C
$\text{Zn}_{0.85}\text{Ge}_{0.15}$	613, 633°C
$\text{Zn}_{0.96}\text{Ge}_{0.04}$	643, 650°C

4. Conclusion

The temperature required to dissolve 1 % silicon was calculated for a range of metal alloys. It became apparent from this work that the most promising alloys were those of

a Type I and Type II metal.

Acknowledgments

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References

- [1] C.D. Thurmond and M. Kowalchik, J. Bell Sys. Tech. 39 (1960).
- [2] K. Leovec and A. Slobodskoy, J. Electrochem 111 (1964) 65.
- [3] R. Hultgren, P.D. Desal, D.T. Hawkins, M. Gleiser and K.K. Kelly, Am. Soc. for Metals (Ohio, 1973).
- [4] B. Girault, F. Chevrir, A. Joullie and G. Bougnot, J. Crystal Growth 37 (1977) 169.