

The Reactive Processing of Silicides

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Interest in silicides as advanced materials for high-performance applications has focused significant attention on the processing of these materials. In recent years, various processing methodologies have been evaluated. This article provides a comprehensive review of reactive processing techniques and the results of various investigations.

INTRODUCTION

Silicides have attracted the attention of researchers due to a combination of interesting properties. The interest in silicide materials dates back to the start of the century when, in 1907, MoSi₂ was proposed as a protective layer for ductile metals.¹ Several years later, the first patent on silicides was issued to Kanthal in 1956 for their "superkanthal" heating elements. These heating elements are used extensively in high-temperature furnaces because they can withstand prolonged exposure in air. The formation of a thin silica layer is attributed to their excellent oxidation resistance.

The low electrical resistivity of silicides in combination with higher thermal stability, electromigration resistance, and excellent diffusion-barrier characteristics is important for microelectronic applications.² Additionally, silicides also possess the necessary attributes for a high-temperature structural material, including a high melting temperature, low density, and good mechanical and microstructural stability from room temperature to the service temperature.³ Potential high-temperature applications include turbine airfoils, burning chamber parts, and missile nozzles.⁴ Table I presents data on melting temperatures, densities, and crystal structures of various silicides.

Conventionally, silicides are processed either by arc melting, silicidation of elemental powders, or reduction of metal oxide. These processes are energy-intensive and require long homogenization times in order to obtain desired products. The loss of silicon by volatilization during arc melting can result in the formation of undesirable intermediate phases. In addition, the silicide powders obtained by these routes have high oxygen contents and other impurities, which are unacceptable for high-temperature structural applications and in the fabrication of microelectronics devices. By utilizing reactive processing techniques such as combustion synthesis (CS), mechanical alloying, displacement reactions, chemical vapor deposition (CVD)

and plasma vapor deposition, high-purity powders can be obtained.

In a reactive process, constituent elements/compounds react in-situ and produce desirable products.⁵ A characteristic parameter of these processes is the state (e.g., solid, liquid, gas, or plasma) at which the in-situ reactions take place. Mechanical alloying and displacement reactions involve reactions in the solid state, while combustion synthesis involves reaction in the liquid state. Reactions occurring as a result of the application of a shock wave can either be in the solid or liquid state. CVD involves the

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reaction of gases and the deposition of resultant products onto a substrate. To the best of our knowledge, plasma processing of silicides has not yet been carried out. However, plasma spraying has been used in the deposition of MoSi₂ and MoSi₂-based coatings.⁶⁻⁸

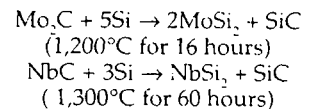
DISPLACEMENT REACTIONS

Displacement reactions are solid-state diffusional reactions between elements and/or compounds to yield thermodynamically stable phases compared to the starting reactants.⁹ These reactions have the ability to produce novel composites with in-situ reinforcements and tailored microstructures. Earlier work on displacement reactions involving metals and oxides was performed by Rapp and coworkers.¹⁰⁻¹¹

The product morphologies in displacement-reaction-processed products are either layered or aggregate. The latter morphology is further subdivided into lamellar or interwoven types. For engineering applications, an interwoven morphology in particulate composites or in the reaction zone (between matrix

and fiber) in fiber-reinforced composites is beneficial to the transfer of stresses and crack-growth resistance.¹¹

Displacement reactions have been applied to the processing of NbSi₃/SiC¹² and MoSi₂/SiC¹³⁻¹⁶ composites. Corresponding diffusion couples were homogenized (at the specified conditions) to yield composites in accordance with the following reactions:



The reaction zones in both diffusion couples exhibited an interwoven morphology and contained a homogenous distribution of SiC particulates with an average size of one micrometer in a matrix of MoSi₂ and NbSi₃, respectively.

The results from the diffusion couples were extended to the fabrication of solid samples. Powder compacts of Mo₃C and silicon were hot pressed at 1,300°C for two hours followed by 1,700°C for one hour.¹³⁻¹⁶ These compacts contained about 30 vol.% of SiC in an MoSi₂ matrix (Figure 1). The SiC particulates were spheroidized with a radius of 1 μm. A densification step at 1,700°C was neces-

Table I. The Physical Properties of Silicides

Silicide	Melting Temp. (°C)	Density (g/cm ³)	Crystal Structure
MoSi ₂	2,030	6.24	C11 ₂
Mo ₃ Si ₂	2,180	8.24	D8 _m
Nb ₃ Si ₂	2,484	7.16	D8 ₃
NbSi ₃	1,930	5.66	C40
Ti ₃ Si ₂	2,130	4.32	D8 ₃
TiSi ₂	1,542	4.04	C54
TiSi	1,570	4.21	B27
Zr ₃ Si ₂	2,210	5.90	D8 ₃
ZrSi ₂	1,520	4.88	C49
ZrSi	2,095	5.56	B27
V ₃ Si ₂	1,973	5.71	A15
V ₂ Si ₃	2,010	5.32	D8 ₃
Vsi ₂	1,673	4.63	C40
Ta ₃ Si ₂	2,450	13.55	C16
Ta ₂ Si ₃	2,505	13.4	D8 ₃
TaSi ₂	2,204	9.08	C40
Cr ₃ Si ₂	1,773	6.46	A15
CrSi	1,475	5.18	B20
CrSi ₂	1,477	4.63	C40
W ₃ Si ₂	2,370	14.5	D8 ₃
Wsi ₂	2,160	9.86	C11 ₂
Re ₃ Si ₂	1,960	14.43	D8 ₃
ReSi	1,880	13.08	B20
ReSi ₂	1,980	10.69	C11 ₂
CoSi	1,460	6.58	B20
CoSi ₂	1,326	4.98	C1
NiSi	992	5.92	B31
NiSi ₂	993	4.83	C1

sary, although the reaction between Mo_2C and silicon proceeded to completion at $1,350^\circ\text{C}$. The final composition in the hot-pressed samples lies in the three-phase field, constituting MoSi_2 -SiC- $\text{Mo}_5\text{Si}_3\text{C}$.

The reaction characteristics and the reaction mechanisms in the formation of MoSi_2 /SiC composites established silicon as the fastest diffusing species.¹⁶ The ternary phase ($\text{Mo}_5\text{Si}_3\text{C}$) was the first to form, followed by the MoSi_2 phase. The SiC phase formed at the interface between the ternary phase and MoSi_2 and grew into the ternary phase. In the case of the formation of NbSi_2 /SiC composites, two possible diffusion paths— NbC/NbSi_2 /SiC/Si and $\text{NbC}/\text{SiC}/\text{NbSi}_2$ /Si—were suggested.¹²

Displacement reactions must be performed in combination with hot pressing or hot isostatic pressing in order to process dense materials. Although displacement reactions have the ability to produce tailored compositions and microstructures, longer times are needed to homogenize the desired product phases. This could be of concern if the process is to be scaled-up for commercial application.

MECHANICAL ALLOYING

Mechanical alloying is an intense high-energy milling process that is used to synthesize intermetallic compounds from elemental powder blends.^{17,18} The process involves repeated fracturing and welding of powders (both metallic and nonmetallic) in a highly energized ball mill (Figure 2). The fracturing of the powders by the grinding media produces clean surfaces, and when these surfaces come in contact they are welded together. The kneading of powders due to repeated fracturing and welding leads to alloying at the atomic level. Intermetallics, composites, and second-phase dispersed alloys with nanometer grain size have been obtained by mechanical



Figure 1. A micrograph of MoSi_2 -SiC composite processed by displacement reaction and thermally etched. The light areas are MoSi_2 and dark areas are SiC.

alloying. The process can also be used to synthesize amorphous alloys. The extension of solid-solubility limits in binary systems and the synthesis of novel phases in some binary systems with limited or no miscibility have been reported.^{17,18}

Several reports on the processing of silicides and silicide composites by mechanical alloying are available in the literature.¹⁹⁻³⁴ Many useful silicides have been synthesized both in the amorphous and crystalline states. Mechanical alloying of transition-metal silicides have been widely investigated as a result of their potential for high-temperature structural applications.^{21,22} The alloying process was nonuniform and different even when the expected compounds (Nb_5Si_3 and Ta_5Si_3) had similar physical properties and crystal structure. In the Ta-Si system, amorphization resulted after alloying for ten hours, while crystalline phases were obtained for niobium and vanadium silicides. In the Nb-Si system, rapid and instantaneous formation of Nb_5Si_3 was observed.^{23,24} No reaction was detected, and the powders remained in their elemental state before this instantaneous transformation. This behavior was attributed to an exothermic reaction between niobium and silicon. The generation of hot spots that subsequently initiate an exothermic reaction during mechanical alloying has been reported previously in the Ni-Al system.²⁵

Similar observations were also reported during the mechanical alloying of MoSi_2 .^{26,27} The abrupt transformation to MoSi_2 occurred between 3–3.25 hours of milling. Traces of unreacted molybdenum were still present. The large negative heat of mixing and stored interfacial energy were responsible for the initiation of a combustion reaction.

Nanocrystalline MoSi_2 and WSi_2 with grain sizes of 10–15 nm synthesized by mechanical alloying were consolidated to above 95 percent of theoretical density at $1,500^\circ\text{C}$, a temperature much lower

than that used for consolidating commercial powders.^{28,29} Despite all the precautionary measures taken to avoid SiO_2 contamination during processing, it was still present at the grain boundaries. An in-situ carbothermal reduction due to carbon addition was able to remove the SiO_2 layer that formed during hot pressing.^{30,31} Besides eliminating the silica layer, carbon additions were also helpful in obtaining in-situ MoSi_2 -SiC composites.

In addition to crystalline materials, amor-

phous silicides were also processed by mechanical alloying in the M-Si system.³²⁻³⁴ In the Ti-Si binary system, mechanical alloying proceeds with the formation of a solid solution of titanium in silicon followed by the formation of amorphous Ti_3Si_3 and TiSi_2 .³² Utilizing a slight variation of ball milling called revolution-step-like decreasing (RSD) mode, it was possible to promote amorphization in some M-Si systems.³³ After milling at high-vial rotation speeds to enhance chemical alloying, the rotation speeds are gradually reduced during subsequent milling stages in the RSD mode. By reducing milling speeds, the nucleation of stable phases is suppressed, thereby, promoting amorphization. Amorphous Ni_2Si , Co_3Si , Mo_3Si , Mn_3Si , and Cr_3Si were processed using the RSD mode.

Although mechanical alloying has proven to be versatile in processing amorphous and crystalline silicides, large-scale production of these materials is yet to be realized. A significant problem with mechanical alloying is the contamination of the powders/products by gases such as oxygen and nitrogen as well as contamination from the vial and the ball. These contaminants can form glassy phases and segregate to the grain boundaries, resulting in poor mechanical properties. While detailed reports exist on the processing and characterization, no details on the mechanisms of formation are currently available. When nanocrystalline materials are obtained by mechanical alloying, care should be taken to retain the nanometer grain size after consolidation in order to fully utilize the benefits of nanometer grain-sized materials. In most systems, mechanical alloying requires a long time to achieve equilibrium and stable phases. This can be overcome by increasing the rate of reaction between the reactants.

COMBUSTION SYNTHESIS

The process that utilizes the exothermic heat of reaction between elements/compounds to synthesize useful intermetallic compounds is referred to as self-propagating high-temperature synthesis (SHS) or combustion synthesis. Upon initiation, the reaction wave propagates from one end of a compact to the other end. As the reaction front passes through the compact, it transforms the reactants to products. A schematic of the combustion synthesis process is shown in Figure 3. Pioneering work on combustion synthesis is credited to Merzhanov and co-workers at the Institute of Chemical Physics in the former Soviet Union.^{35,36} Demonstrated advantages of the CS process include the utilization of a simple reactor, a very low energy requirement, the ability to simultaneously synthesize and densify the product, tailored micro-

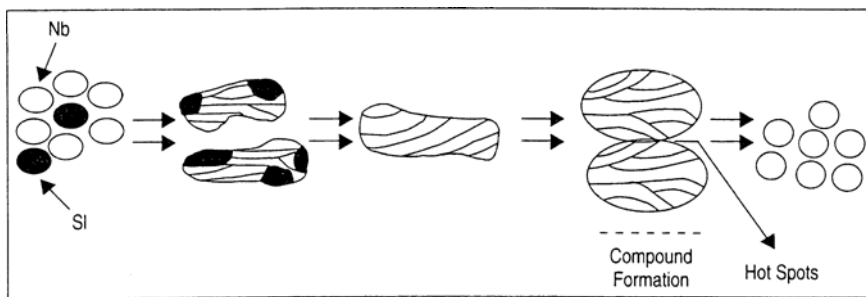


Figure 2. A schematic of the mechanical alloying process.²⁴

structures and properties, higher purity of the products as compared to reactants, and the synthesis of metastable phases.³⁵⁻³⁸ A significant disadvantage is the generation of pores and cracks due to the violent nature of the reaction.

Combustion reactions take place either in the self-propagating mode or the thermal explosion mode. A self-propagating reaction occurs when the reaction is initiated locally in the compact and propagates as a wave front through the compact. In the explosion mode, the powder compact is heated in a furnace until combustion occurs simultaneously in the whole compact.^{37,38} An assessment based on the thermodynamic principles is needed to ascertain whether a reaction will occur in the propagating mode. Such an analysis is available for a number of silicides.³⁹

Combustion reactions are influenced by the density and diameter of the green compact, reactant particle size, processing atmosphere, amount of diluent additions, and the stoichiometric ratio of the reactants. The effect of these parameters on the combustion synthesis of silicides has been reported by Sarkisyan et al.⁴⁰ and Azatyan et al.⁴¹ Generally, with an increase in particle size and compact density and a lowering of compact diameter, the combustion velocity and combustion temperature are lower, thereby, rendering the reactions incomplete.

The first report on the CS of silicides was preliminary in nature.⁴² Among silicides, MoSi₂ and Ti₃Si₂ have been extensively studied with respect to their processing by the combustion synthesis route. Stoichiometric MoSi₂ and Ti₃Si₂ have been obtained by igniting a compact of stoichiometric elemental mixtures.⁴³⁻⁴⁹ Compact diameters of 20 mm and greater are needed to ensure a complete conversion of reactants and to obtain single-phase MoSi₂ and Ti₃Si₂.

Theoretical calculations of the adiabatic temperature for MoSi₂ indicate that this reaction is on the border of being self-propagating. To ensure completeness of the reaction, the synthesis of MoSi₂ has been carried out in the thermal-explosion mode^{50,51} and the chemical-oven approach in addition to the self-propagation mode.⁴⁴⁻⁴⁶ Preheating of the reactants or the presence of inert atmo-

sphere results in higher combustion temperatures and combustion velocities.^{45,46} Quenching experiments established the formation of MoSi₂ in a single step during CS, while differential thermal analysis established two reaction mechanisms for the formation of MoSi₂.⁴⁴ With lower heating rates (<100°C/min.), a solid-state reaction to form Mo₂Si₃ is followed by a reaction between Mo₂Si₃ and molten silicon to yield MoSi₂. At higher heating rates (>100°C/min.), a liquid silicon-solid molybdenum reaction occurs, leading to the formation of MoSi₂. The latter is typical of a combustion reaction.

Similarly, single-phase Ti₃Si₂ has been processed in the self-propagating mode in an inert atmosphere.^{40,41,48,49} Intermediate phases (TiSi, Ti₅Si₃) and oxides (SiO₂, TiO₂) may form in addition to Ti₃Si₂ when combustion is performed in air.⁴⁰ Diluent additions up to 25 wt.% of Ti₃Si₂ or 15 wt.% of SiC additions to Ti + 0.6Si maintain the stability of the combustion wave. Although stable combustion was achieved, the addition of SiC altered the reaction mechanism, leading to substantial amounts of TiSi₂, Ti₅Si₃, and SiO₂ being present in addition to Ti₃Si₂.⁴⁹

Combustion synthesis has also been used to obtain in-situ precipitated second-phase dispersants in a metallic/intermetallic matrix. This process is referred to as the XDTM, a trademark of Martin Marietta Corporation.⁵² In this process, constituent elements of the desired ceramic are mixed with the matrix material and heated in a furnace. Once the desired temperatures are achieved, the ceramic dispersant forms due to an exothermic reaction amongst its constituents. The XD process offers the flexibility to incorporate up to 95 wt.% ceramic in a metallic/intermetallic matrix. Examples of composites produced by the XD process include TiB₂/Al, MoSi₂/Al, TiB₂/Co, and ZrB₂/Al.⁵⁶

MoSi₂ composites with TiB₂, ZrB₂, HfB₂, and SiC reinforcements have been processed by the XD process.⁵³⁻⁵⁵ The mechanical properties at room and elevated temperatures were found to be significantly higher for the XD-reinforced composites.

Recently, the incorporation of an electric field during the combustion reaction to transform a sluggish reaction into one

that is self-sustaining has been reported by Munir and coworkers.⁵⁶⁻⁵⁸ This technique has been referred to as field-assisted combustion synthesis (FACS). By applying an electric field, completion of the reaction is ensured and the necessity to preheat the sample is eliminated. Using FACS, MoSi₂ composites with varying amounts of SiC,⁵⁶ niobium,⁵⁷ and ZrO₂⁵⁸ particulate reinforcements have been fabricated. Refined microstructures were obtained due to higher cooling rates in FACS. The composites contained only the matrix and the reinforcing phases. This is of significant interest, especially in the MoSi₂-Nb composite, as other possible phases such as niobium silicide were not detected in the composite.

While considerable work has been carried out on the CS of silicides, detailed elucidation of the reaction mechanisms has yet to be performed. These studies need to be performed in order to obtain a better understanding of the synthesis of various silicides. A significant issue that has not yet been addressed is the processing of dense silicide materials by CS. It is necessary to incorporate a densification step following combustion if dense materials are to be obtained. Reaction hot isostatic pressing is one such approach that has been able to produce dense MoSi₂ from elemental reactants.⁵⁹ It has been claimed that the XD process can be incorporated into conventional processing techniques such as rolling, forging, extrusion, and machining to produce near-net shapes.⁵² These fabrication steps could introduce defects in the composites such as porosity, compositional inhomogeneity, stress cracking, and orientation of the grains.

SHOCK SYNTHESIS

The application of a high-energy shock wave to induce reactions in a mixture of powders forms the basic foundation of the shock synthesis process. The use of shock compression for initiating solid-state chemical reactions and for material

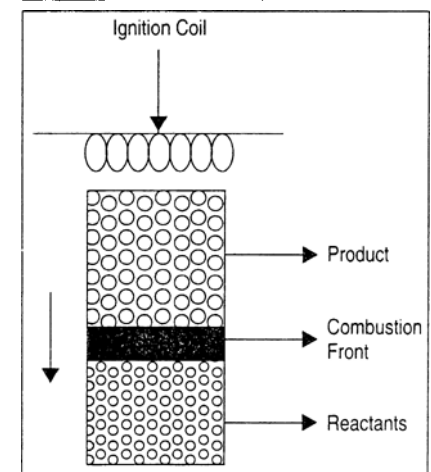


Figure 3. A schematic illustration of the combustion synthesis process.

synthesis was a natural outgrowth of the work on shock-induced phase transformation.⁶⁰ Shock compression of elemental powder mixtures can lead to chemical reactions resulting in the formation of equilibrium and nonequilibrium compounds. Shock application on powder mixtures results in extensive plastic deformation, fluid-like turbulent flow, particle comminution, and the mixing of constituents with fresh and clean surfaces. In addition, irreversible changes in the starting composition, volumetric distribution of constituents, and shape of the void space are affected as a result of shock compression. Shock processes are best described in terms of departures from equilibrium and can be classified into two types—shock-assisted and shock-induced reactions.⁶¹

Chemical reactions occurring in shock-modified powder mixtures are termed shock-assisted reactions. Shock-assisted reactions are initiated due to bulk temperature increases that occur on the time scale of thermal equilibrium, but at times significantly greater than for pressure equilibrium. It has been shown that particle morphology can change as a result of shock treatments, thus, resulting in higher diffusivities.⁶² Potential uses for shock-assisted reactions are the sintering of difficult-to-consolidate oxides and non-oxide ceramics, improving the catalytic activities of materials, and enhanced kinetics of nucleation of precipitating phases.

Shock-induced reactions are those that are limited to, and occur within, the time scales associated with pressure equilibrium. Shock-induced reactions are difficult to monitor experimentally, since they occur with relatively small changes in bulk properties.

Shock synthesis has been used to process silicides in the Nb-Si, Mo-Si, Ti-Si, and Ni-Si systems.⁶³⁻⁶⁶ Recovery experiments in the Nb-Si and Mo-Si systems revealed fully reacted, partially reacted, and unreacted regions.⁶⁴ Fully reacted regions were characterized by the presence of large pores/voids, while the unreacted regions were consolidated to near theoretical density. Reacted regions were characteristic of a completely reacted, melted, and resolidified material. The extent of shock-synthesis reaction increases with an increase in shock en-

ergy, temperature, and the enthalpy of the reaction.^{64,65}

Recently, Thadhani⁶⁶ reported the effect of particle-size distribution on the overall efficiency of shock synthesis in the formation of Ti₃Si₂. Reactions were favorable under certain combinations of porosity and particle sizes. The effect of residual air in the processing chamber during the shock synthesis of Ti-Si mixtures has also been reported. It was observed that when residual air was present, the reactions were induced at lesser threshold energies. The requirement of threshold energy for the initiation of shock-induced reaction was first proposed by Krueger et al.⁶⁶ According to this requirement, no reaction is possible below a certain threshold energy. This was later modified based on the assumption that a steady-state reaction can propagate if the energy generated due to a chemical reaction is greater than the energy dissipated from the system.⁶⁶

Based on electron microscopic observations, Meyers et al.⁶⁶ proposed a self-sustaining mechanism for the formation of niobium silicides and molybdenum silicides. The reaction is initiated at the interface between niobium and silicon. After initial solidification, the product is spherulized due to surface tension forces and eventually squeezed out into the interface, thus, exposing a newer surface for the reaction to initiate. As a result, a constant metal-molten silicon interface is maintained at all times.

Reaction mechanisms in shock-modified powders are different from those occurring in unshocked powders. The nature of the reaction depends on the morphology of the powders used.⁷⁰ Coarse/rounded morphology mixtures react mostly in the liquid state, while flaky powders react completely in the solid state. In fine powders, a large solid-state reaction and limited liquid-state reaction is observed. In the Ni-Si system,⁶⁷ shock-compressed powders exhibit a solid-state reaction, resulting in stoichiometric products. The increased solid-state diffusivity is attributed to the presence of defects, shorter diffusion distances, more intimate particle contacts, and the formation of fresh and clean surfaces.

Although significant research has been carried out, many issues remain to be

resolved. It is also not clear if the reactions are completed during the microsecond duration of shock compression. The micromechanisms responsible for chemical reactions in powder mixtures are not yet well established. While the role of plastic deformation, defects, and local hot spots are believed to be important, experimental verification of mechanisms for rapid mass-transport remains an outstanding issue. Conflicting opinions also exist about the state of material prior to the onset of the reaction.

CHEMICAL VAPOR DEPOSITION

CVD is a process wherein products from a chemical reaction in the vapor phase are deposited onto a heated surface.⁷¹ The process is versatile and can be used to coat materials in order to improve wear resistance, corrosion resistance, strength, and electrical conductivity. The most attractive feature of CVD is its ability to deposit thin films in crevices and deep recesses such as those encountered in electronic circuits. Silicide coatings on silicon are widely employed in the semiconductor industry to improve electrical resistivity.⁷²

Prior to conducting CVD in any system, it is necessary to evaluate the various process parameters such as precursor, deposition temperature, substrate temperature, and substrate material with the help of thermodynamic principles. By choosing a ratio of the precursors, it is possible to evaluate the stability of the material to be coated. It is essential for the coating to be thermodynamically stable with the substrate and not decompose into other compounds. Thermodynamic analysis can predict the optimum processing conditions to achieve the desired coating.

For the deposition of silicides, the source of silicon has been either SiH₄, SiH₂Cl₂, or SiCl₄, and the source of the metal (W, Ti, Ta, Nb, or Mo) has been its corresponding fluorides or chlorides. The various precursors used for depositing each silicide and their processing conditions are listed in Table II.

As stated previously, the characteristics of the silicide films that are deposited are influenced by a number of variables. These include substrate temperature, deposition temperature, pressure, and the ratio of the precursors. Substrate cleanliness is very important in order to prevent any difficulties during subsequent processing steps such as annealing or contact metallization. Surface cleaning using freonTM and silane^{80,81} has been applied before deposition of tungsten silicide and titanium silicide, respectively. With surface cleaning, the films had the desired properties as well as the ability to withstand post-deposition thermal treatments.

The necessity to select a proper pre-

Table II. Chemical Vapor Deposition Conditions for Various Silicides

Silicide	Precursor	Deposition Temperature	Deposition Pressure	Reference
MoSi ₂	MoF ₆ and SiH ₄	250–300°C	<2 torr	71
MoSi ₂	MoCl ₅ and SiH ₄	650–950°C	0.6–2.0 torr	76
TaSi ₂	TaCl ₅ and SiH ₄	400–500°C	1–2 torr	71
TiSi ₂	TiCl ₄ and SiH ₄	825°C	150 m torr	74
TiSi ₂	TiCl ₄ and SiH ₄	720–780°C	1.2 m torr	75
TiSi ₂	TiCl ₄ and Si	850°C	<1 torr	71
WSi ₂	SiH ₄ and WF ₆	350°C	<1 torr	71
WSi ₂	SiH ₂ Cl ₂ , WF ₆ , and H ₂	550–650°C	0.5–1 torr	77
WSi ₂	WF ₆ and Si ₂ H ₆	290–300°C	Atm.	78
NbSi ₂	Si ₂ Cl ₆ and NbCl ₅	500–600°C	0.3–1 torr	73

cursor system is best illustrated by considering the CVD of tungsten silicide. Initially, tungsten silicide was deposited from tungsten hexafluoride and silane.⁷¹ These films resulted in a high-fluorine concentration with poor film adhesion and degradation of properties during annealing. By replacing silane with dichlorosilane, it was possible to overcome these problems and achieve tungsten silicide (WSi_x , $2.2 < x < 2.6$) films with good conformity and adherence.^{77,79,82-85} Stresses develop in the as-processed films due to the mismatch in the coefficient of thermal expansion between the film and the substrate. Subsequent annealing is necessary to relieve these stresses. In some instances, the decrease in stress levels is associated with changes in the resistivity levels.⁷⁹ The composition and crystal structure of the films influenced the mechanical properties obtained. In tungsten-silicide films, the resistivity and the amount of stresses were dependent on the silicon content in the as-deposited films.⁷⁷

In addition to the literature cited, the enormous amount of literature available on the CVD of silicides suggests a sustained interest in these materials. In certain systems, a good handle on the processing variables has enabled researchers to deposit good, clean, and desired deposits. In others, the stoichiometry of the products deposited is not uniform. During the annealing of films, changes in resistivity occur; correlations need to be developed between changes in resistivities and stress relieving. A precise methodology to arrive at the desired resistivity upon annealing is yet to be established. Also, very little is known on the mechanisms of formation of the various silicides.

ACKNOWLEDGEMENTS

This work was supported in part by a grant from the National Science Foundation (DMR9315057) and by Basic Energy Sciences under U.S. Department of Energy (DOE) contract DE-AC06-76RLO 1830 with Pacific Northwest Laboratory, which is operated for the DOE by Battelle Memorial Institute. R. Radhakrishnan acknowledges the support of a Battelle Pacific Northwest Laboratory Energy Research Fellowship.

References

1. A.K. Vasudevan and J.J. Petrovic, *Mater. Sci. & Eng.*, A155 (1992), p. 1.
2. S.P. Murarka, *Silicides for VLSI Applications* (New York: Academic Press), 1983.
3. P.J. Meschter and D.S. Schwartz, *JOM*, 41 (11) (1989), pp. 52-55.
4. R. Rosenkranz, G. Frommeyer, and W. Smarsly, *Mater. Sci. & Eng.*, A152 (1992), p. 288.
5. R.R. Rice, *Ceram. Eng. Sci. Proc.*, 11 (1990), p. 1226.
6. R. Tiwari, H. Herman, and S. Sampath, *High Temperature Ordered Intermetallic Alloys IV*, ed. L.A. Johnson, D.P. Pope, and J.O. Stiegler (Pittsburgh, PA: MRS, 1991).
7. R.G. Castro et al., *Scripta Met. Mater.*, 26 (1992), p. 207.
8. Y.L. Jeng, J. Wolfenshine, and E.J. Lavernia, *Scripta Met. Mater.*, 28 (1993), p. 453.
9. R.A. Rapp, A. Ezis, and G.J. Yurek, *Met. Trans.* 4 (1973), p. 1283.
10. G.J. Yurek, R.A. Rapp, and J.P. Hirth, *Met. Trans.*, 10A (1979), p. 591.
11. C. Tangchitvitaya, J.P. Hirth, and R.A. Rapp, *Met. Trans.*, 13A (1982), p. 585.

12. C.R. Kao, J. Woodford, and Y.A. Chang, *Mater. Sci. & Eng.*, A195 (1995), p. 29.
13. C.H. Henager, Jr., J.L. Brimhall, and J.P. Hirth, *Scripta Met. Mater.*, 26 (1992), p. 585.
14. C.H. Henager, Jr., J.L. Brimhall, and J.P. Hirth, *Mater. Sci. & Eng.*, A155 (1992), p. 109.
15. C.H. Henager, Jr., and J.L. Brimhall, *Scripta Met. Mater.*, 26 (1993), p. 1597.
16. C.H. Henager Jr., J.L. Brimhall, and L.N. Brush, *Mater. Sci. & Eng.*, A195 (1995), p. 65.
17. C.C. Koch, *Ann. Rev. Mater. Sci.*, 19 (1989), p. 121.
18. C. Suryanarayana, *Bibliography on Mechanical Alloying and Milling*, (Cambridge, U.K.: Cambridge International Science Publishing, 1995).
19. G. Le Caer et al., *J. Mater. Sci.*, 25 (1990), p. 4726.
20. D.L. Zhang and T.B. Massalski, *J. Mater. Res.*, 9 (1994), p. 53.
21. R.K. Viswanadham, S.K. Mannan, and S. Kumar, *Scripta Met. Mater.*, 22 (1988), p. 1011.
22. K.S. Kumar and S.K. Mannan, *High Temperature Ordered Intermetallic Alloys III*, ed. C.T. Liu et al. (Pittsburgh, PA: MRS, 1992), p. 415.
23. J. Kajuch, J.D. Rigney, and J.J. Lewandowski, *Mater. Sci. & Eng.*, A155 (1992), p. 59.
24. J. Kajuch and K. Vedula, *Advances in Powder Metallurgy*, (1990), p. 187.
25. M. Atzmon, *Solid State Powder Processing*, ed. A.H. Clauer and J.J. Barbadillo (Warrendale, PA: TMS, 1990), p. 173.
26. S. Patankar, S-Q. Xiao, and J.J. Lewandowski, *J. Mater. Res.*, 8 (1993), p. 1311.
27. E. Ma et al., *J. Mater. Res.*, 8 (1993), p. 1836.
28. R.B. Schwarz et al., *Mater. Sci. & Eng.*, A155 (1992), p. 75.
29. G.T. Fei et al., *J. of Alloys and Compounds*, 229 (1995), p. 280.
30. S. Jayashankar and M.J. Kaufman, *J. Mater. Res.*, 8 (1993), p. 1428.
31. S. Jayashankar and M.J. Kaufman, *Scripta Met. Mater.*, 26 (1992), p. 1245.
32. A. Calka et al., *J. Mater. Sci. Lett.*, 10 (1991), p. 734.
33. K. Omura and H. Miura, *Appl. Phys. Lett.*, 60 (1992), p. 1433.
34. I. Okadome, K. Unno, and T. Arakawa, *J. Mater. Sci.*, 30 (1995), p. 1807.
35. A.G. Merzhanov and I.P. Borovinskaya, *Combust. Sci. and Tech.*, 10 (1975), p. 195.
36. A.G. Merzhanov, *Combustion and Plasma Synthesis of High Temperature Materials*, ed. Z.A. Munir and J.B. Holt (New York: VCH, 1992), p. 1.
37. Z.A. Munir, *Ceram. Bull.*, 67 (1988), p. 342.
38. Z.A. Munir and V. Anselmi-Tamburini, *Mater. Sci. Rep.*, 3 (1989), p. 277.
39. S.B. Bhaduri, Z.B. Qian, and R. Radhakrishnan, *Scripta Met. Mater.*, 30 (1994), p. 179.
40. A.R. Sarkisyan et al., *Comb. Expl. Shock Waves*, 15 (1979), p. 310.
41. T.S. Azatyan et al., *Comb. Expl. Shock Waves*, 15 (1979), p. 35.
42. V.I. Itin et al., *Sov. Phys. Journal*, 18 (1976), p. 408.
43. S.B. Bhaduri, R. Radhakrishnan, and S. Wojcicki, *Advances in Powder Metallurgy*, vol. 9, ed. J.M. Capus and R.M. German (Princeton, NJ: APMI, 1992), p. 369.
44. S.C. Deevi, *Mater. Sci. and Eng.*, A149 (1992), p. 241.
45. S.C. Deevi, *J. Mater. Sci.*, 26 (1991), p. 3343.
46. S. Zhang and Z.A. Munir, *J. Mater. Sci.*, 26 (1991), p. 3685.
47. S.B. Bhaduri, R. Radhakrishnan, and Z.B. Qian, *Scripta Met. Mater.*, 29 (1993), p. 1089.
48. J. Trambukis and Z.A. Munir, *J. Am. Cer. Soc.*, 73 (1990), p. 1240.
49. A.K. Bhattacharya, *J. Am. Cer. Soc.*, 74 (1991), p. 2707.
50. J. Subrahmanyam and R. Mohan Rao, *J. Am. Cer. Soc.*, 78 (1995), p. 487.
51. J. Subrahmanyam and R. Mohan Rao, *Mater. Sci. and Eng.*, A183 (1994), p. 205.
52. J.M. Brupbacher, L. Christodoulou, and D.C. Nagle, U.S. patent 4,710, 348 (1987).
53. R.M. Aikin, Jr., *Ceram. Eng. Sci. Proc.*, 12 (1991), p. 1643.
54. J. Cool et al., *Eng. Sci. Proc.*, 12 (1991), p. 1656.
55. E.W. Lee et al., *JOM*, 43 (3) (1991), pp. 54-57.
56. S. Gedavanishvilli and Z.A. Munir, *Scripta Met. Mater.*, 31 (1994), p. 741.
57. A. Feng and Z.A. Munir, *J. Appl. Phys.*, 76 (1994), p. 1927.
58. I.J. Shon and Z.A. Munir, *Mater. Sci. and Eng.*, A202 (1995), p. 256.
59. D.A. Hardwick, P.L. Martin, and R.J. Moores, *Scripta Met. Mater.*, 27 (1992), p. 391.
60. P.S. DeCarli and J.C. Jamison, *Science*, 133 (1961), p. 1821.
61. N.N. Thadhani, *J. Appl. Phys.*, 76 (1994), p. 2129.
62. E. Dunbar et al., *Proc. AIRAPT/APS High Pressure Science and Technology Conference*, ed. S.C. Schmidt (New York: AIP Press, 1994).
63. M.A. Meyers et al., *Mater. Sci. and Eng.*, A201 (1995), p. 150.
64. L.H. Yu and M.A. Meyers, *J. Mater. Sci.*, 26 (1991), p. 601.
65. K.S. Vecchio, L.H. Yu, and M.A. Meyers, *Acta Met. Mater.*, 42 (1994), p. 701.
66. M.A. Meyers, L.H. Yu, and K.S. Vecchio, *Acta Met. Mater.*, 42 (1994), p. 715.
67. S.C. Deevi and N.N. Thadhani, *Mater. Sci. and Eng.*, A192/193 (1995), p. 604.
68. B.R. Krueger, A.H. Muntz, and T. Vreeland, Jr., *Met. Trans.* A, 23A (1992), p. 55.
69. N.N. Thadhani, private communication.
70. E. Dunbar, N.N. Thadhani, and R.A. Graham, *J. Mater. Sci.*, 28 (1993), p. 2903.
71. H.O. Pierson, *Handbook of Chemical Vapor Deposition* (New Jersey: Noyes Publications, 1992).
72. A. Sherman, *Chemical Vapor Deposition for Microelectronics—Principles, Technology and Applications* (New Jersey: Noyes Publications, 1992).
73. W.S. Cheng and C.Y. Lee, *J. Mater. Sci. Lett.*, 13 (1994), p. 1204.

74. G.J. Reynolds, G.B. Cooper III, and P.J. Gaczi, *J. Appl. Phys.*, 65 (1989), p. 3212.
75. K. Saito et al., *J. Electrochem. Soc.*, 141 (1994), p. 1879.
76. S. Inoue et al., *J. Electrochem. Soc.*, 130 (1983), p. 1603.
77. S.C. Telford et al., *Appl. Phys. Lett.*, 62 (1993), p. 1766.
78. D. Dobkin et al., *J. Electrochem. Soc.*, 137 (1990), p. 1623.
79. R.S. Nowicki et al., *J. Vac. Sci. and Tech.*, A9 (1991), p. 1073.
80. K. Saito et al., *J. Electrochem. Soc.*, 141 (1993), p. 513.
81. K. Saito, T. Amazawa, and Y. Arita, *Jap. J. Appl. Phys.*, 29 (1990), p. L185.
82. S. McClatchie, H. Thomas, and D.V. Morgan, *Appl. Surf. Sci.*, 73 (1993), p. 58.
83. T. Hara, T. Miyamoto, and T. Yokoyama, *J. Electrochem. Soc.*, 136 (1989), p. 1177.
84. T. Hara et al., *J. Electrochem. Soc.*, 137 (1990), p. 2955.
85. S.G. Telford et al., *J. Electrochem. Soc.*, 140 (1993), p. 3689.

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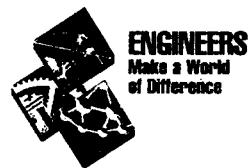
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