

The Low Temperature Synthesis of Vanadium Selenides Using Superlattice Reactants

Milo Overbay, Thomas Novet, and David C. Johnson¹

Department of Chemistry and Materials Science Institute, University of Oregon, Eugene, Oregon 97403

Received August 23, 1995; in revised form February 23, 1996; accepted February 28, 1996

Traditional exploration of phase diagrams is dominated by the annealing of reaction products formed from high temperature reactions. In this paper we present an alternative approach, based on the low temperature crystallization of amorphous reaction intermediates, which is ideally suited for the study of incongruently melting compounds. Within the vanadium selenium phase diagram we demonstrate the ability to prepare the incongruently melting compounds V_2Se_9 and V_5Se_4 using the average composition of the amorphous reaction intermediate to control phase nucleation. We also present evidence for a new, kinetically stable vanadium selenide near the composition $V_{0.8}Se$ which disproportionates into a mixture of VSe_{2-x} and V_5Se_4 upon annealing at 500°C. The compounds V_3Se_8 and V_3Se_4 were not observed to nucleate from any of the amorphous intermediates, regardless of their overall composition. © 1996

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INTRODUCTION

The traditional approach to the preparation of solid state compounds involves the direct reaction of stoichiometric amounts of the elements via a solid-state reaction. This approach typically initially involves relatively high reaction temperatures to facilitate the interdiffusion of the reactants, followed by annealing. Traditional, high temperature synthesis methods yield products thermodynamically stable under the reaction conditions. Unfortunately ternary compounds thermodynamically unstable with respect to binary compounds and many compounds stable only at low temperatures are not accessible via this synthetic approach. For example, no attempt to prepare incongruently melting compounds by a rapid (relative to the diffusion rate) cooling of a high temperature system will succeed, since the compounds in question do not exist above their melting point and the diffusion rates are slow in the temperature range in which they are stable. A carefully designed cooling sequence involving long annealing times at low temperatures is required to prepare such compounds

via a direct solid state reaction. This requires some prior knowledge of the phase diagram, including the positions of the eutectics closest to the phase in question, to optimize the cooling sequence and other reaction conditions (1, 2).

Much recent effort in solid state synthesis has been directed at the low temperature synthesis of compounds, in part due to the traditional dominance of high temperature methods in preparing new materials. Low temperature synthesis methods allow the preparation of many new compounds and structure types which are metastable or unstable at higher temperatures. Low temperature synthesis is typically accomplished by using low temperature eutectics as solvents for the reactants or through the use of hydrothermal growth conditions. These exploratory synthesis efforts depend to a large degree upon intuition and insight, since very little is known concerning the reaction mechanisms, the higher order phase diagram of the product, or the even more complex reacting systems that include the fluxes used. While it is difficult to predict or control the structure of the products from these synthesis techniques, they have yielded many interesting new structure types, particularly those containing polychalcogenide anions (3).

Our synthetic efforts have focused on the use of superlattice reactants, which are designed to form amorphous alloys at low temperatures which we then use as metastable reaction intermediates for the preparation of solid state compounds (4). This synthesis approach separates long range interdiffusion from crystallization. Long range interdiffusion of the reactants occurs in the formation of the amorphous alloy and is driven by the steep concentration gradients in the superlattice reactant (5). Nucleation of the final crystalline product, a kinetic phenomenon, is then the rate limiting step in the synthesis (6). This separation of these reaction steps presents an ideal synthetic approach to compounds stable only at low temperatures as they can form directly from the amorphous alloy. Since this crystallization only involves local rearrangements of the atoms in the amorphous alloy, compound growth is not limited by the slow diffusion rates found at low temperatures. In addition, the composition of the amorphous alloy

¹ To whom correspondence should be addressed

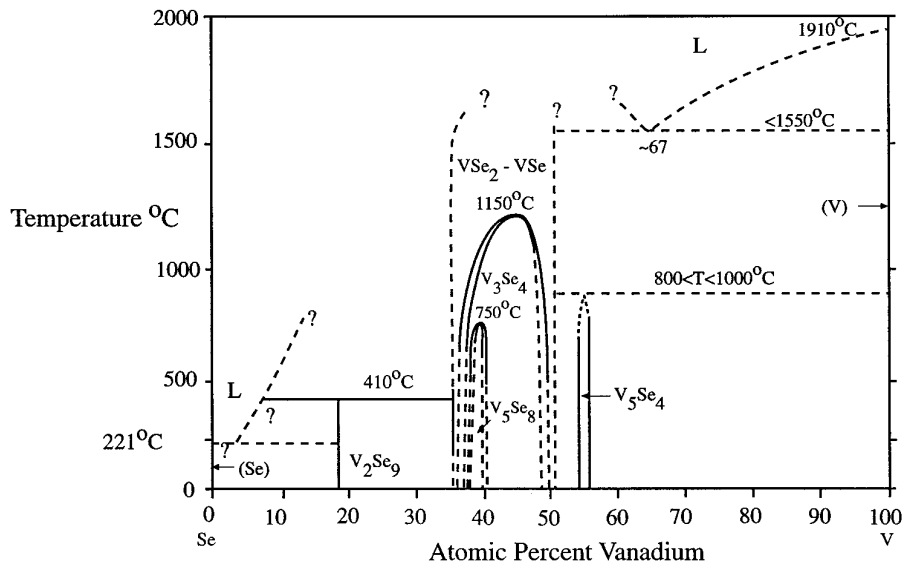


FIG. 1. The vanadium-selenium phase diagram (11).

can be used to control compound nucleation, for example favoring ternary compound formation relative to binary phase formation from a ternary amorphous intermediate (7).

Synthetically, the difficulties with this approach are forming a homogeneous amorphous alloy of a particular composition and then controlling the nucleation of this intermediate to the desired product. We have chosen to use superlattices as our initial reactants, since the ability to continuously vary the dimensions of the repeating unit down to an Ångstrom length scale allows the interdiffusion time and temperature to be optimized (8). The regular structure of the superlattice also produces a diffraction pattern which contains information as to the electron density distributions within the repeating unit (9). As this multilayer is gently interdiffused, the disappearance of these superlattice reflections with temperature and time permits the interdiffusion process to be quantified and interfacial structures to be observed (5). The energetics of diffusion and subsequent nucleation can be measured via differential scanning calorimetry (10).

In this paper we use this approach to study the reaction of vanadium-selenium superlattices, demonstrating the utility of this approach in preparing incongruently melting compounds at low temperatures and the ability to control nucleation of compounds via the composition of the amorphous intermediate. The vanadium-selenium system (Fig. 1) was chosen for this study because it contains three composition regions of interest for testing the utility of this synthetic approach. The three composition regions of interest are the metal rich side of the phase diagram, containing the phase V_5Se_4 , which has a limited range of solid solution and disproportionates above $800^\circ C$ into vanadium and

VSe ; the selenium rich side of the phase diagram, containing the line compound V_2Se_9 , which is stable only below $410^\circ C$, incongruently melting to form selenium and VSe_2 above that point; and a complicated region between VSe_2 and VSe containing several compounds with overlapping stoichiometries and temperature stability ranges (11). In each of these regions we will determine the reaction mechanism as a function of the layer thickness of the repeating unit and address whether we can control the formation of the known binary compounds by preparing a superlattice with the desired layer thicknesses and overall composition.

EXPERIMENTAL SECTION:

Synthesis of samples. Samples were made in a custom-built ultra-high-vacuum chamber with independently controlled sources. Vanadium was deposited as $0.5 \text{ \AA}/\text{sec}$ by an electron-beam gun that was controlled via a Leybold-Inficon XTC quartz crystal thickness monitor. Selenium was deposited with a temperature-controlled Knudsen cell. The rate of selenium deposition, approximately $1.0 \text{ \AA}/\text{sec}$, was monitored on a quartz crystal thickness monitor. Above each of the sources were computer-controlled shutters to allow precise control of elemental layer thicknesses (12). Samples were deposited on silicon substrates polished to $\pm 3 \text{ \AA}$ rms for X-ray studies and on silicon wafers coated with poly(methylmethacrylate) for DSC studies.

Grazing- and high-angle x-ray diffraction. X-ray data were collected on a Scintag 2000 theta-theta diffractometer modified for low angle diffraction measurement (13). Grazing-angle x-ray diffraction data were used to confirm the layered structure of the starting superlattice

and to determine the layer spacing. High-angle diffraction data were used to determine whether a film contained crystalline elements or compounds.

Differential scanning calorimetry (DSC). The heat produced and absorbed by the diffusion, nucleation, and decomposition of the V–Se samples was measured using a Du Pont TA9000 DSC module. Approximately 1 mg of sample free of the substrate was used in this experiment. The sample was obtained by first coating a 4-in. silicon wafer with poly(methyl methacrylate) (PMMA). This was done using a 3% solution of PMMA in chlorobenzene and a spincoater rotating at 1000 rpm. The desired V–Se layers were then deposited on the substrate. A piece of the deposited substrate was then placed in acetone, which dissolved the PMMA and left the sample floating free. The sample, which typically broke into small pieces, was gathered by sedimentation into an aluminum DSC pan. Excess acetone was dried off under vacuum, and then the pan was crimped closed.

The sample was placed in the DSC with an empty aluminum pan as a reference. The sample was heated to 600°C at a rate of 10 C/min. under flowing nitrogen. This obtained the irreversible changes that occurred during the initial heating. The sample was cooled and reheated to 600°C twice more to obtain baselines for the reversible changes in the sample. A comparison of the two baselines gives a measure of the repeatability of the experiment. The net heat absorbed or released from the multilayer samples was obtained from the difference between the first and the subsequent runs.

Thermogravimetric analysis (TGA). Thermogravimetric analysis was used to determine the actual stoichiometry of the original layered sample. A sample was floated off the PMMA-coated substrate and dried. A known mass of sample was then heated to 550°C in the TGA system in flowing air and held at this temperature for at least thirty minutes. The mass change on oxidation of the vanadium to V₂O₅ and volatilization of the selenium was then used to determine the composition of the original sample.

RESULTS AND DISCUSSION

Table 1 contains a summary of the 12 samples prepared as part of this investigation. Two samples were prepared on the metal rich side of the phase diagram, six samples were prepared on the selenium side of the phase diagram, and four samples were prepared between these two extremes. Most of the sample were prepared with 5Å vanadium layers with the selenium thickness adjusted to obtain the desired stoichiometries, except for the metal rich sample A-1, which had 25Å vanadium layers, and sample B-3, which had 4Å vanadium layers, and insufficient sample to determine the stoichiometry by oxidizing the sample.

The structure of the as-deposited films was determined

TABLE 1

A Summary of Intended Elemental Layer Thicknesses, Measured Thicknesses of the Repeating Units, and Measured Compositions of the Samples from Thermogravimetric Analysis for the Vanadium–Selenium Multilayer Samples Prepared in This Study

Sample	Intended vanadium thickness (Å)	Intended selenium thickness (Å)	Measured thickness (Å)	TGA determined V/Se Ratio
A-1	25	30	54	1.42
A-2	5	10		1.04
B-1	5	13	19	0.83
B-2	5	15	21	0.85
B-3	4	10	14.4	—
C-1	5	23	30	0.61
D-1	5	30	39	0.37
D-2	5	36	39	0.23
D-3	5	41	42	0.27
D-4	5	43	54	0.32
D-5	5	57	58	0.20
E-1	5	70	80	0.19

using X-ray diffraction. The lack of diffraction maxima in the high angle diffraction pattern of the as-deposited samples indicates that the samples were amorphous with respect to X-ray diffraction. The low-angle diffraction patterns of the as-deposited samples all contained Bragg diffraction maxima from the modulation of the elements during deposition. A typical low angle diffraction pattern of an initial superlattice reactant, shown in Fig. 2, contained Bragg diffraction maxima out to approximately ten degrees, indicating that the interfaces contain Fourier components with wavelengths less than 10 Å setting a maximum width for the mixing of the elements. The diffraction data combined with the thin vanadium layers used in most of the samples, imply that their composition essentially modulates between regions which are relatively vanadium rich and regions which are vanadium poor. This mixing at the interfaces on deposition hinders crystallization of the elemental layers. Subsidiary maxima, resulting from the interference of X-rays scattered from the front and back surfaces of the superlattice reactant as well as incomplete destructive interference from the internal interfaces, were also observed between the Bragg maxima. Typically, these subsidiary maxima were observed out to 3 degrees suggesting that the elemental layers have roughness on the order of 5Å, as variations in layer thickness and/or roughness increasingly broaden the subsidiary maxima with increasing angle (14).

By indexing the low angle diffraction patterns to a one-dimensional unit cell, the thicknesses of the repeating bilayer units can be determined. For all of the samples studied, the measured thickness of the repeating bilayer units

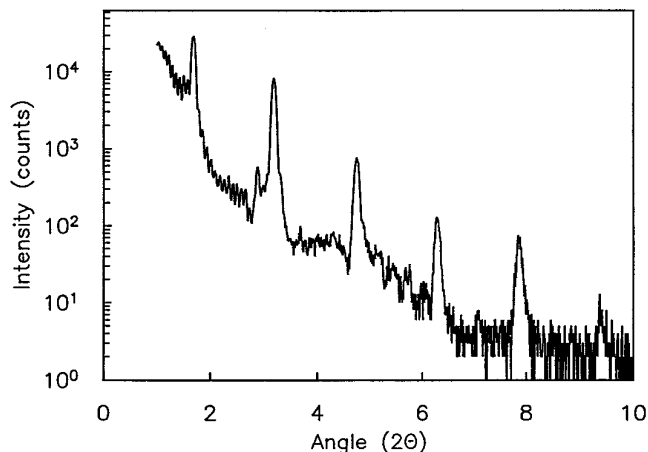


FIG. 2. The low angle diffraction pattern of a vanadium-selenium multilayer A-1 containing 25 Å of vanadium and 30 Å of selenium. The diffraction maxima result from elemental modulation of the multilayer. The decay of the intensities of the Bragg orders with increasing angle implies that significant interdiffusion of the layers has occurred during the deposition process. The disappearance of subsidiary maxima in between the main Bragg features at 2θ approximately 3° implies that there is significant roughness at the interfaces between the vanadium and selenium.

were within several angstroms of the intended thicknesses as summarized in Table 1. The measured compositions determined using TGA were proportional to the ratio of the intended vanadium thicknesses divided by the selenium thicknesses to within the errors expected from the reproducibility of the deposition monitors. The largest errors occurred for samples D-2-D-4, which were prepared sequentially, and may have resulted from accidental displacement of a quartz crystal monitor within the chamber as a crystal was being replaced.

Reactions of superlattices with compositions more vanadium rich than VSe: Formation of V_5Se_4 . The evolution of the initially modulated and amorphous reactants was followed using both differential scanning calorimetry and X-ray diffraction. The heat evolved as a function of temperature was measured using differential scanning calorimetry for the two metal rich samples. The trace of the most metal rich sample studied (A-1) is shown in Fig. 3. It contains a broad low-temperature exotherm which ends by 250°C , followed by a sharp exotherm with a maximum heat flow at 375°C . The calorimetry trace of sample A-2 was similar, with the sharp exotherm shifted to 310°C . To determine structural changes associated with these exothermic transitions, diffraction data were collected on a second portion of the sample which was also ramped at $10^\circ\text{C}/\text{min}$. in the calorimetry cell to the temperatures above and below the sharp exotherm. No Bragg diffraction peaks due to elemental modulation were observed in the low angle diffraction after annealing the sample at 250°C . The high angle diffrac-

tion data, shown in Fig. 4, indicate that the sample remained amorphous with respect to X-rays during the initial broad exotherm. After the sharp exotherm, the high angle diffraction pattern of both samples indicate that they have formed V_5Se_4 . The small excess of vanadium in sample A-1 and the excess of selenium in sample A-2 could not be detected in the diffraction patterns and the lattice parameters of the V_5Se_4 product in both samples were constant, suggesting that only slight variations in composition are likely.

The calorimetry data, combined with the diffraction data, suggest a reaction pathway we have observed previously for reactants with thin elemental layers, in which the initial layered reactant first interdiffuses, forming an amorphous intermediate. Nucleation of this amorphous intermediate is then the rate limiting step in forming the crystalline compound (6). The temperature of the maximum heat flow resulting from crystallization varies with the composition of the amorphous intermediate. The maximum in the heat flow resulting from crystallization in the sample with a composition of 5 moles of vanadium to 3.5 moles of selenium occurs at 375°C , while in the sample with a composition of 5 moles of vanadium to 4.8 moles of selenium the maximum heat flow occurs at 310°C . This sensitivity of the nucleation temperature to composition gives in principle the ability to control the compound formed using the composition of the amorphous intermediate (10).

Reactions of superlattices with compositions between VSe and VSe_2 . As can be seen in Fig. 1, this region of the

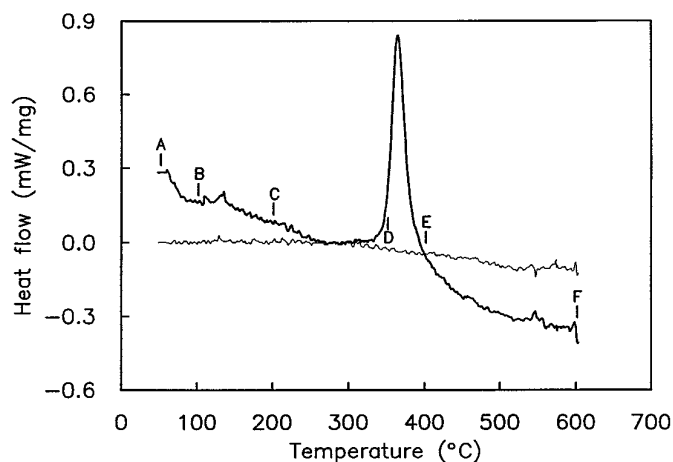


FIG. 3. Heat flow as a function of temperature for vanadium-selenium superlattice A-1 containing 30 Å of Se and 25 Å of V in the repeating unit, leading to an overall stoichiometry of approximately 5 moles of vanadium to 3.6 moles of selenium. The maximum in the heat flow at 375°C corresponds to an exotherm. Diffraction data (Fig. 4) were collected after a second portion of the sample was ramped at $10^\circ\text{C}/\text{min}$. to the temperatures indicated by the capital letters.

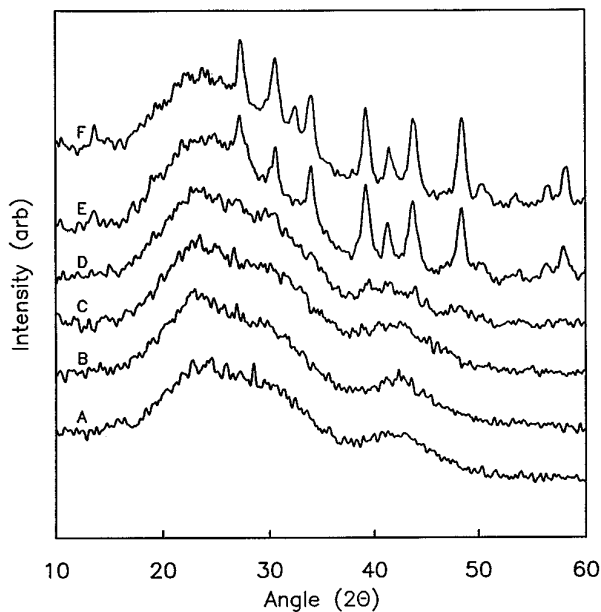


FIG. 4. The diffraction patterns as a function of temperature obtained at the temperatures indicated in Fig. 3 for sample A-1. The diffraction scans are offset for clarity. The lack of diffraction maxima in scans A, B, and C indicates that the sample is X-ray amorphous. Diffraction scans E and F contain the expected diffraction maxima for the compound V_5Se_4 as given in the JCPDS diffraction files. Diffraction scan D, taken just after the onset of the exotherm in Fig. 3, contains small diffraction maxima where strong diffraction maxima for V_5Se_4 are expected, indicating that V_5Se_4 has nucleated.

phase diagram is very complicated, containing several compounds with complex structures which are stable only at low temperatures beneath a solid solution region at higher temperature. Since the stoichiometries of several of the compounds overlap, composition alone cannot be used to control stoichiometry. We found that samples prepared with initial vanadium layer thickness greater than 10\AA in this composition range did not have sharp exotherms in the differential scanning calorimetry data. Diffraction data collected as a function of annealing temperature and time indicates that heterogeneous nucleation of VSe_{2-x} occurs at low temperatures (approximately 200°C) in these samples. All of the samples studied in this composition window with 5\AA vanadium layer thicknesses, however, reacted to initially form an amorphous intermediate. The subsequent crystallization of the amorphous intermediate divides these samples into two classes.

Three samples (B-1, B-2, and B-3) showed sharp exotherms at 180°C in DSC scans, as shown in Fig. 5. X-rays taken at several temperatures, shown in Fig. 6, indicate that the samples are amorphous and no longer layered before the exotherm and form a crystalline compound after the exotherm. The simple diffraction pattern obtained after the exotherm is similar to that previously reported for

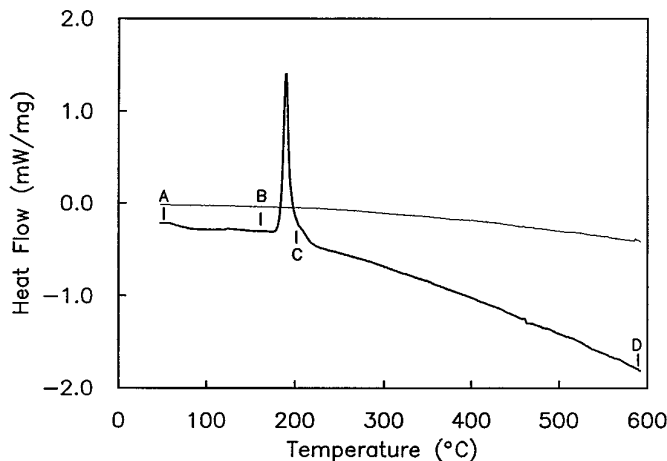


FIG. 5. Heat flow as a function of temperature for vanadium-selenium superlattice B-1 containing 13\AA of Se and 5\AA of V in the repeating unit, leading to an overall stoichiometry of approximately 5 moles of vanadium to 6 moles of selenium. The maximum in the heat flow at 180°C corresponds to an exotherm. Diffraction data (Fig. 6) were collected after a second portion of the sample was romped at $10^\circ\text{C}/\text{min}$. to the temperatures indicated by the capital letters.

VSe_{1+x} , but the lack of $00l$ with l odd suggests either higher symmetry or smaller unit cell than this conventional form (15-17). As shown in Fig. 6, heating to 600°C transforms the sample into VSe_{2-x} mixed with a small amount of V_5Se_4 . Work is continuing in this area to improve the crystallinity

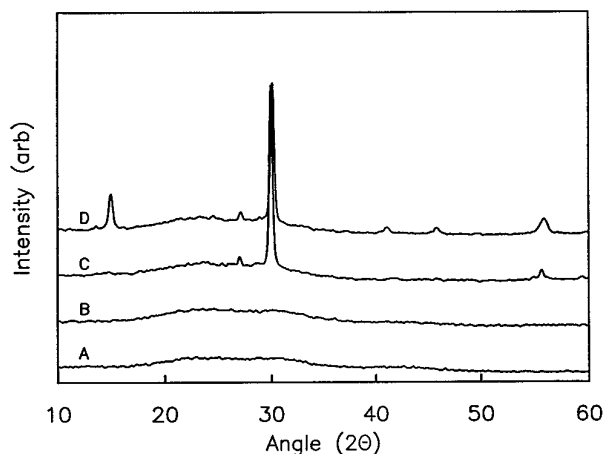


FIG. 6. The diffraction patterns as a function of temperature obtained at the temperatures indicated in Fig. 5 for sample B-1. The diffraction scans are offset for clarity. The lack of diffraction maxima in scans A and B, taken before the exotherm in Fig. 5, indicate that the sample is X-ray amorphous. The peaks in diffraction scan C, taken after the exotherm in Figure 5, indicates that the sample has crystallized. This phase does not correspond to a known vanadium selenide. The diffraction maxima in diffraction scan D correspond to those expected for the compound VSe_2 as given in the JCPDS diffraction files.

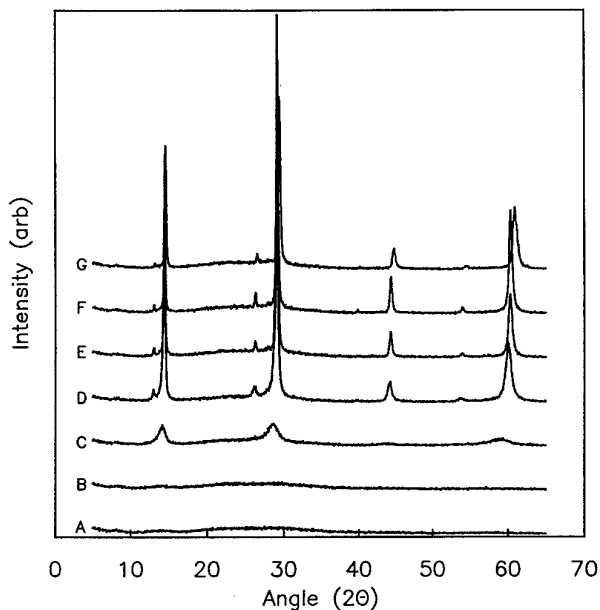


FIG. 7. The diffraction patterns as a function of temperature obtained in sample C-1 (A—25°C, B—100°C, C—150°C, D—300°C, E—380°C, F—420°C, G—600°C). The diffraction scans are offset for clarity. The lack of diffraction maxima in scans A and B, taken before the 130°C exotherm, indicate that the sample is X-ray amorphous during this initial annealing. Diffraction data collected at 150°C (scan C) indicate that VSe_{2-x} forms during the 130°C exotherm. Diffraction data collected on further annealing show the subsequent formation of V_5Se_4 . On heating to 600°C there is a distinct decrease in the c -axis lattice parameter of the VSe_{2-x} compound formed.

and phase purity of samples containing the simple V–Se structure to facilitate determining its structure.

Moving to the more selenium rich samples, we observed a second sequence of phase evolution typified by sample C-1 which had an overall thickness of 30 Å and a nominal composition of 1.64 moles of selenium to each mole of vanadium. The differential scanning calorimetry trace of this sample contained a sharp exotherm at 130°C. Diffraction data collected as a function of annealing time and temperature as shown in Fig. 7 show that VSe_{2-x} formed after the 130°C exotherm, followed by the subsequent formation of V_5Se_4 after further heating of the sample to 300°C. We suspect that V_5Se_4 forms in the regions enriched in vanadium as the VSe_{2-x} crystallites grow. On heating to 600°C there is a distinct decrease in the c -axis lattice parameter of the VSe_{2-x} compound formed.

Reactions of superlattices with compositions more selenium rich than VSe_2 : The formation of V_2Se_9 . The vanadium–selenium phase diagram (Fig. 1) shows that the compound V_2Se_9 decomposes peritectically at 410°C, forming VSe_2 and selenium. Consequently, the reported synthesis of V_2Se_9 involves 3 months of heating at less than 410°C combined with periodic grinding of the reaction mixture

(18). The extended annealing period of the reported synthesis is necessary to interdiffuse the reactants because the reactant particle sizes are macroscopic. In addition to the slow diffusion rates at 400°C, the reaction rate is additionally slowed by the formation of VSe_2 as the initial product at the selenium–vanadium interfaces.

The samples prepared in this composition range as part of this investigation all contained 5 Å vanadium layers and displayed two distinct reaction pathways depending upon the thickness of the selenium layers. The sample with the thickest selenium layers, E-1, corresponding to a composition of 5.3 moles of selenium for each mole of vanadium, formed VSe_2 between 220°C and 350°C without an obvious crystallization peak in DSC scans. The 00 l orientation of the crystallites suggests that the VSe_2 crystallites nucleated at and grew along the vanadium–selenite interface. The sample remained VSe_2 as the temperature was ramped at 10°C/minute, gradually losing the excess selenium with increasing temperature.

SUMMARY

The results in both the metal rich region investigated, where we formed V_5Se_4 and the selenium rich region where we formed V_2Se_9 indicate that the multilayer reactants are a promising approach for the synthesis of compounds which are stable only at low temperatures. The separation of interdiffusion and nucleation in this synthetic approach led to well formed crystalline products at low temperatures. Compound growth is not limited by the slow diffusion rates found at low temperatures as crystallization only involves local rearrangements of the atoms in the amorphous alloy. To some extent, composition of the amorphous alloy can be used to control which crystalline product will nucleate. The reproducible formation of a new compound near stoichiometry $VSe_{1.2}$, which decomposed by 600°C, also suggests that this approach provides a new avenue for exploring the low temperature region of phase diagrams. Superlattice reactants provide the opportunity to travel “up” a phase diagram, from low temperature to high temperature. This is the reverse of conventional synthetic approaches which typically rely upon cooling to produce crystalline products.

The results reported herein also suggest that techniques need to be developed which give control over the structure formed. This ability is especially important in systems which have several polymorphs stable at the same composition or which have several different compounds stable in a narrow composition window. In the present study, the compounds V_5Se_8 and V_3Se_4 were not observed to nucleate from any of the amorphous intermediates, regardless of their composition. The failure of these compounds to form might result from the relatively large crystallographic unit cells of these compounds relative to the VSe– VSe_2 solid

solution. This might lead to higher nucleation energies for these compounds relative to the crystallography more simple solid solution. One approach toward this end is to develop the ability to “seed” nucleation to obtain the desired product. Work toward this goal is currently in progress.

ACKNOWLEDGEMENTS

This work was supported by the National Science Foundation (Grants DMR-9213352 and DMR-9308854). Additional support by the Office of Naval Research (Grant N0014-93-1-0205), the University of Oregon, and the U. S. Department of Education Graduate Assistance in Areas of Need Program (TN) is gratefully acknowledged.

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