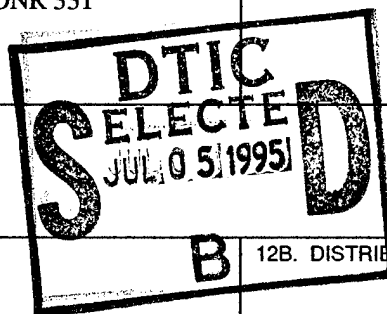


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The Synthesis of Crystalline Superlattices by Controlled Crystallization of Modulated Reactants

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ABSTRACT

A series of new crystalline superlattice compounds containing an integral number of intergrown dichalcogenide layers were prepared through controlled crystallization of Ti/Se/Nb/Se superlattice reactants. Discussed in this paper are two members of this series containing seven dichalcogenide layers (3 NbSe₂, 3 TiSe₂ and one mixed layer) and twelve dichalcogenide layers (6 NbSe₂ and 6 TiSe₂ layers) oriented with the dichalcogenide layers parallel to the substrate surface. The synthesis of these new compounds begins with the design and preparation of an elementally modulated reactant. The component elemental layer thicknesses and annealing sequence are chosen to favor interfacial nucleation of the component binary compounds. The evolution of the initially layered reactants into the crystalline superlattices was monitored as a function of temperature using x-ray diffraction. The layered reactants contract in the c-axis direction during an initial low temperature anneal as NbSe₂ and TiSe₂ crystallites nucleate and grow along the interfaces, kinetically trapping the desired superlattice structure. The crystalline domains become more aligned with additional annealing at higher temperatures, as crystal growth of domains with the c-axis oriented perpendicular to the substrate surface is favored. The c-axis domain size increases gradually as a function of annealing time and temperature yielding high quality c-axis oriented TiSe₂/NbSe₂ crystalline superlattices after annealing at 500°C. The large number of observed 00 l diffraction orders permits the crystal structure of the superlattice in the c-axis direction to be determined using Reitveld analysis. The rational synthesis of intergrowth

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compounds from superlattice reactants using this approach extends the range of heterostructures which can be prepared. This permits the tailoring of physical properties as a function of compositional layer thicknesses and native properties of the parent compounds.

Many advances in technology - for example higher electronic device speeds,^{1, 2} low threshold current semiconductor lasers, "band gap engineering" of materials^{3, 4} fundamentally new physical phenomena such as the quantum Hall effect⁵ and the fractional quantum Hall effect⁶ have resulted from the ability to prepare heterostructures with defined compositions on a nanometer length scale. To produce these structurally tailored materials researchers have developed several synthesis techniques based upon layer by layer epitaxial growth. These techniques all involve sequential exposure of the growing crystal surface to fluxes of the components. The substrate is typically heated to optimize the surface mobility of the components and the flux rates are carefully controlled to compensate for the relative sticking coefficients of the component species. Many different techniques have been used to supply the reactants to the growing crystal, including evaporation, sputtering and chemical vapor deposition. Most prominent among these techniques is molecular beam epitaxy in which molecular beams of the constituent elements are directed toward the growing crystal surface under conditions which have been determined to result in epitaxial growth of the desired structure. By alternating between different molecular beams, the composition of the growing film can be controlled and varied on length scales as short as 5-10 Ångstroms. Liquid and solid phase epitaxial growth techniques have also been developed to prepare modulated structures, however the length scales on which the composition can be modulated are typically a factor of ten larger than those achieved with molecular beam epitaxy.⁷

Within heterostructure superlattices, interfaces constitute a large fraction of the total material. In semiconductors, where defect and impurity concentrations dominate electrical properties, controlling interfacial quality is crucial in device manufacture. The low background pressures and epitaxial nature of interfaces resulting from molecular beam epitaxial growth leads to heterostructures with exceedingly low impurity and defect densities, important parameters to control in device applications. Epitaxial growth limits the disorder normally found at the interfaces but it greatly restricts the range of superlattice components. While the development of strained layer epitaxy⁸ and Van der Waals epitaxy^{9, 10} has reduced the stringent lattice matching requirement for epitaxial growth, lattice matching of the components of a heterostructure remains

an important synthetic parameter. In addition to lattice matching, the growth conditions for the component materials of a superlattice must also be compatible. Since epitaxial growth depends upon controlling the composition at the growing surface, this becomes increasingly difficult to control as the number of elements in the heterostructure compounds increase.

This paper describes an alternative approach to the production of new heterostructures which is not based upon epitaxial growth. Instead it is based upon the kinetic trapping of the desired crystalline superlattice from the solid state reaction of an elementally modulated reactant. In spirit, this approach parallels that of an organic chemist who might carefully synthesize two reactant molecules to be coupled using kinetic control in the key reaction step in the synthesis of a large natural product. In the work described herein, instead of two molecules, we prepare interwoven layers of the elements within a superlattice reactant. The layer sequence and thicknesses are chosen based upon mechanistic studies of the initial stages of the solid state reactions between the binary components. Low temperature annealing nucleates the binary compounds at interfaces. These crystallites grow along the interfaces, kinetically trapping the desired superlattice structure. This synthetic approach provides advantages for the preparation of heterostructures containing ternary compounds and for non-latticed matched systems, which would be difficult to prepare using synthetic approaches based upon epitaxial growth. The new compounds described in this paper consist of intergrowths of two-dimensional transition metal dichalcogenides.

Heterostructures of the transition metal dichalcogenides were attractive targets for several reasons. Synthetically, the extensive experience in our laboratory exploring the effects of composition and layer thicknesses on interfacial reactivity in transition metal-selenium systems provided the inspiration and the mechanistic background information necessary to design the initial reactants.¹¹⁻¹³ We suspected that the two dimensional, layered structure found in these compounds might also facilitate the preparation of compositionally abrupt interfaces. Additionally, heterostructures of these dichalcogenides would provide the opportunity to study the interplay between the length scale of the individual layers in the heterostructure and a host of physical

phenomena. The dichalcogenides display a wide range of electrical properties depending on the transition metal ranging from semiconducting to metallic behavior.^{14, 15} The reactivity of the dichalcogenide heterostructures is also of interest, as there exists a well developed low temperature chemistry involving intercalation of molecular species into the Van der Waals gaps of these layered materials.^{16, 17} Dichalcogenide heterostructures would present a unique opportunity to explore the effects of superlattice structure on intercalation phenomenon such as staging - the selective intercalation of every n^{th} layer.

The idea for this synthetic approach to heterostructures evolved from experimental results obtained while examining the early stages of the reaction between elemental niobium and selenium layers. As shown in Figure 1, we observed the formation of a crystalline product, NbSe₂, after extended low temperature annealing while the sample was still compositionally modulated. The crystalline NbSe₂ product was oriented with its crystallographic c-axis parallel with the layering direction. The diffraction and differential scanning calorimetry data suggest that the NbSe₂ product nucleates at and grows along each reacting planar interface. We observed the interfacial formation of NbSe₂ over a wide composition range and a broad range of layer thicknesses. Reference to the phase diagram shows that other solid state compounds are thermodynamically more stable than a mix of the elements and NbSe₂ at these compositions, suggesting that the initial formation of NbSe₂ at the interface is a kinetic phenomenon. Extended annealing resulted in the ratio of compounds expected by the phase diagram, confirming that NbSe₂ is only a kinetic reaction intermediate.

The reaction mechanism suggested by these results - interfacial nucleation and oriented crystal growth of the kinetic product NbSe₂, produced intriguing possibilities when extended to the reaction of the more complicated initial superlattice reactant shown in Figure 2. Extending this reaction mechanism to the ternary superlattice suggests that the respective dichalcogenide products should each nucleate and grow along the reacting metal-selenium interfaces upon low temperature annealing. The nucleation of a solid solution or ternary product would be hindered by the slow diffusion of the niobium and titanium through the intervening selenium layers. After the interfacial

nucleation, further annealing should result in the dichalcogenide heterostructure shown as the kinetically trapped product.

We tested the proposed reaction sequence by preparing a series of superlattice reactants with the overall structure shown in Figure 2 with varying thicknesses and number of niobium and titanium layers. The composition of each niobium-selenium and titanium-selenium period was chosen to be that of the desired dichalcogenide compounds and the thicknesses were chosen to be integral multiples of the known crystallographic unit cells so that there would be no elemental reactants left in the superlattice after extended annealing. The evolution of the high angle and low angle diffraction patterns of a sample with 3.5 NbSe₂ layers and 3.5 TiSe₂ layers as a function of annealing temperature is shown in Figure 3. The low angle diffraction data indicates that the compositionally modulated nature of the sample persists throughout annealing. The broad diffraction maxima evident at high angles upon low temperature annealing results from the nucleation of the dichalcogenide layers. Differential scanning calorimetry data collected on this sample showed the continual evolution of heat with increasing temperature until 500°C, indicative of the continued growth of the dichalcogenide crystallites. The diffraction patterns show the continuous evolution of the high angle 00 l Bragg diffraction peaks as the dichalcogenide nuclei grow.

Diffraction data was then collected on a sample which was deposited directly upon a silicon wafer containing the appropriate masses of the elements to form 6 NbSe₂ layers and 6 TiSe₂ layers. Rocking curve diffraction scans of the (0 0 12) superlattice diffraction peak taken as a function of annealing temperature show a narrowing with increasing annealing time and temperature, with the half widths decreasing from greater than 3 to 0.56 degrees. This indicates that the superlattice is gradually evolving into the desired, kinetically trapped crystalline superlattice with the 00 l diffraction planes aligned parallel with the initial interfaces present in the superlattice reactant. After annealing this sample at 500°C for 197 hours, the diffraction pattern contains many well resolved diffraction maxima, as shown in Figure 4. All of the diffraction maxima in the diffraction patterns can be indexed as 00 l diffraction maxima resulting in a c-axis lattice parameter

consistent with 6 NbSe₂ layers and 6 TiSe₂ layers in the repeating unit of the superlattice sample. The diffraction pattern is qualitatively what is expected for the intended structure consisting of the convolution of the super-cell diffraction on top of that expected for the dichalcogenides. We were very surprised by the high quality of this diffraction pattern given the amorphous nature of the initial superlattice reactant.

To determine the structure perpendicular to the layering direction, we searched for and found the 10ℓ diffraction intensity in reflection mode on a single crystal diffractometer for a sample annealed for 10 hours at 500°C. The diffraction signal consisted of a ring of intensity indicating well formed dichalcogenide layers that are not uniformly oriented in the *ab* plane due to multiple domains. This is consistent with interfacial nucleation of the layers as suggested in the mechanism shown in Figure 2, whereas epitaxial growth would result in a preferred orientation of the *ab* plane relative to the substrate. As order in the plane perpendicular to the *c* axis develops, the ring of intensity should evolve into a hexagonal pattern of intensity. Observing all of the expected $62\ 00\ell$ diffraction orders between 1 and 80 degrees, however, highlights the well formed structure which develops along the *c*-axis as the superlattice structure is kinetically trapped.

The standard treatment of diffraction in superlattice materials is to consider the superlattice as a perturbation effect on top of the original structures of the components.¹⁸ In this approach, the superlattice diffraction peaks are indexed as $\pm n$ relative to the main diffraction maxima in the component materials. Frequently, the observation of these maxima are used mainly as proof that a superlattice structure exists. The quality of the 00ℓ diffraction data shown in Figure 4 permitted us to gain further insight into the structure of our superlattices by considering the structure as being composed of a single large unit cell, which consists of multiple units similar to those of the parent structures. We refined the positions and occupancies of the atoms using Reitveld analysis.¹⁹ The curve under the data points in Figure 4 is a calculated diffraction pattern for the structure along the *z*-axis (shown in Figure 5) which resulted from least squares analysis of this data.

The refined structure the crystalline superlattice contains the expected structural components based upon the structure of the initial multilayer reactant, and is shown in Figure 5. As designed,

the structure contains 6 layers of titanium diselenide and 6 layers of niobium diselenide with interlayer distances bracketed by those found in polytypes of the pure dichalcogenides. Refining the occupancies of the metals in the layers we find little titanium in the niobium layers compared with niobium in the titanium layers. This can be rationalized using the coordination differences of the metals, as titanium is always octahedral in the dichalcogenides but niobium's coordination can be either octahedral or trigonal prismatic. At the boundary between the niobium and titanium dichalcogenides we find one layer with significant mixed metal population. The van der Waals gaps in both the niobium and titanium dichalcogenide regions are comparable to those found in the pure dichalcogenides. Significantly, the gap between the titanium and niobium dichalcogenides is slightly larger resulting from the a-axis mismatch between the dichalcogenide components.

Several annealing experiments were conducted to probe the rate and extent of interdiffusion of the metal atoms within the superlattices. At 500°C we observed crystal growth but little intermixing of the different metal layers. When we increased the temperature to 600°C we observed slow intermixing of titanium and niobium containing dichalcogenide layers. Raising the temperature to 650°C resulted in the complete intermixing of the metal layers within 12 hours, destroying the superlattice periodicity as the dichalcogenide solid solution forms. This suggests that the layered structures are not equilibrium phases but are only kinetically stable at low temperatures. Since $T\Delta S$ increases with increasing temperature, intermixing the metals is favored at higher temperatures. These structures cannot be prepared by traditional synthetic methods such as direct reaction of the elements at high temperatures as they are thermodynamically unstable.

The growth sequence observed is far from equilibrium as we kinetically trap the desired superlattice products. Understanding the reaction mechanism is crucial to extending this approach to new superlattice materials. Based upon analysis of diffraction data collected as the superlattice is formed, our working hypothesis of the reaction mechanism has an initial interdiffusion of the elements along the interfaces followed by interfacial nucleation of the binary components, as shown in Figure 2. These crystals grow in an oriented manner due to the asymmetric nature of the initial reactant. Grains misoriented relative to the initial layering must be smaller than those which

grow along the layers. Oswald ripening of the grains therefore leads to an increasingly more oriented material with increasing annealing time. Annealing at higher temperatures leads to the mixing of the metals and the destruction of the superlattice. While this model is conceptually easy to extend to many reacting systems, further studies investigating the reaction mechanism of other systems are required to ascertain its general applicability.

The ability to prepare intergrowth compounds from superlattice reactants as described will permit the tailoring of physical properties as a function of compositional layer thicknesses and native properties of the parent compounds as done previously for compound semiconductors. Successful synthesis will depend upon designing an initial superlattice reactant which favors nucleation and crystal growth of the component structures rather than intermixing of the components. Since this approach follows a distinctly different reaction pathway than layer-by-layer epitaxial growth, using superlattice reactants presents significant advantages for the preparation of intergrowths of ternary compounds, heterostructures of compounds with incompatible MBE growth conditions and intergrowths of compounds with significant lattice mismatch.

An interesting question to pose is what determines whether a superlattice product is a composite or a new compound. Obviously, on a micron length scale one has a composite material in which the physical properties result from the component compounds. As the length scale of the compositional modulation decreases to a few Ångströms, a transition from composite behavior to that of a new compound should occur in which observed physical properties do not derive from the component compounds. The exact length scale at which this transition occurs will depend on the property being measured. Exploring the evolution of properties throughout this transition region presents an important opportunity to gain insight into the design of materials with desired properties. Such research is multidisciplinary in nature, presenting significant challenges in the synthesis of new materials with designed structures, determining the atomic structure (particularly through the transition region between materials), and in the measurement of the physical

properties. Controlled crystallization of superlattice reactants provides an additional synthetic route to these materials and increases the variety of compounds which can be intergrown.

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FIGURE CAPTIONS

Figure 1: The evolution of the low angle and high angle diffraction patterns as a function of annealing temperature of a niobium-selenium superlattice prepared by sequentially depositing 9 Ångstroms of niobium and 29 Ångstroms of selenium on a polished silicon substrate (a = 159°C, b = 360°C, c = 518°C, d=600°C). The low angle diffraction pattern contains information regarding the chemical modulation produced by the sequential deposition. It decays with annealing as the niobium and selenium interdiffuse, reducing the chemical modulation. The high angle diffraction pattern shows the continuous growth of 00ℓ diffraction maxima of NbSe₂ as the sample is annealed.

Figure 2: The suggested reaction pathway of a superlattice reactant containing alternating niobium and titanium layers each separated by intervening layers of selenium. On low temperature annealing, the as-deposited layers (a) begin to interdiffuse (b).

Continued annealing results in interfacial nucleation (c) and lateral growth of the respective binary components (d), kinetically trapping the desired superstructure as the final product (e).

Figure 3: Diffraction data collected on a superlattice reactant in which elemental layers were deposited of appropriate thickness to yield 3.5 NbSe₂ layers and 3.5 TiSe₂ layers in the final product. The sample was deposited upon a polymer coated substrate and removed from this substrate by dissolving the polymer. The resulting particles were then annealed at the indicated temperatures in an oxygen free environment. Diffraction pattern a is that of the as-deposited sample, b is after annealing 2 hours at 200°C, c is after annealing 2 hours at 350°C and d is after annealing 2 hours at 500°C. The lattice parameter of the superlattice is 43.472 ± 0.005 Å after annealing at 500°C.

Figure 4: Diffraction data collected on a superlattice reactant in which elemental layers were deposited of appropriate thickness to yield 6 NbSe₂ layers and 6 TiSe₂ layers in the final product. This sample has been annealed a total of 197 hours at 500°C. All of the diffraction maxima can be indexed as 00 l lines of the superlattice as indicated. The curve under the data points is a calculated diffraction pattern obtained from a least squares Reitveld structural refinement resulting in the structure shown in Figure 5.

Figure 5: The refined structure after annealing a total of 197 hours at 500°C for the superlattice unit cell containing 6 NbSe₂ layers and 6 TiSe₂ layers. Indicated next to the respective layers are the percent occupancy of each of the metals and the interlayer and intralayer spacing between selenium layers. The intralayer spacing for the niobium and titanium layers bracket those observed in the binary

compounds. There is a distinct change in interlayer van der Waals spacing through the interface region between the niobium diselenide and titanium diselenide blocks resulting from the a-axis mismatch between the dichalcogenide components.

RELATIVE INTENSITIES

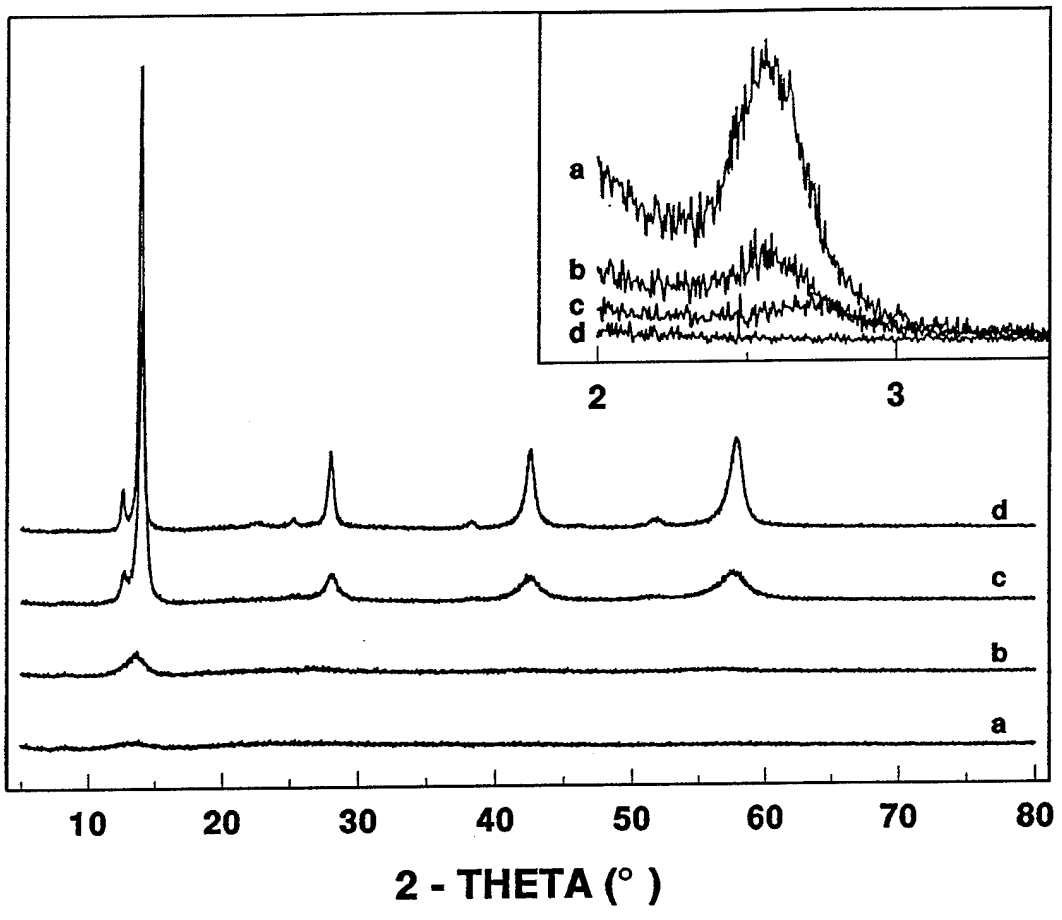


Fig. 1

- a: 50°C
- b: 70°C
- c: 80°C
- d: 100°C

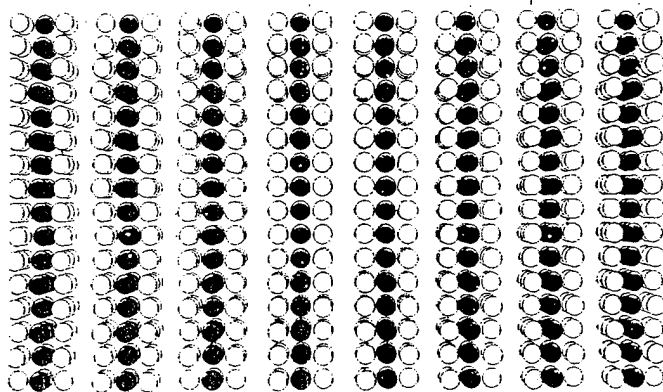
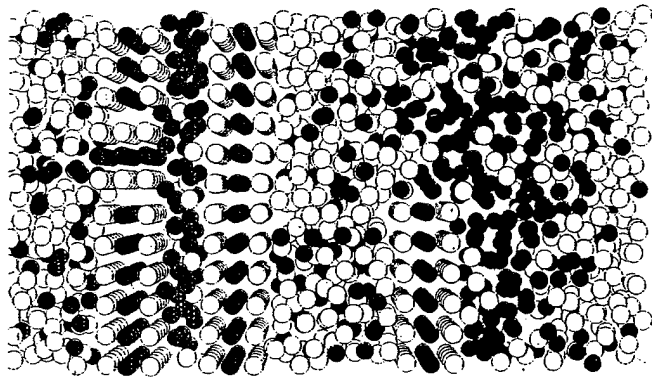
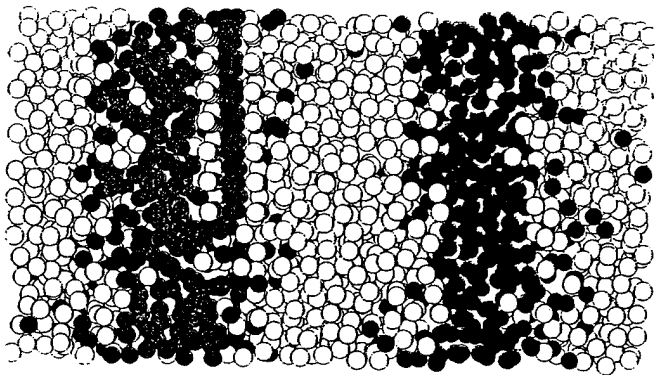
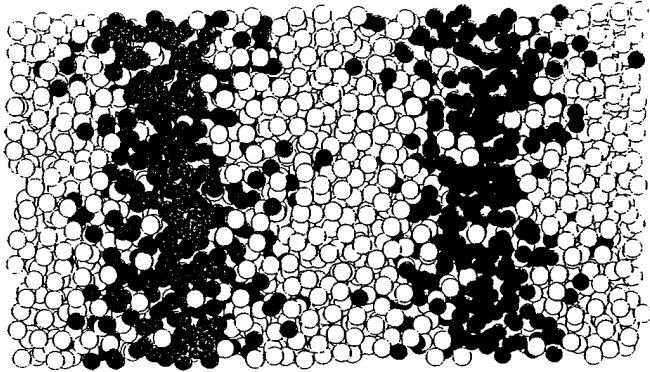
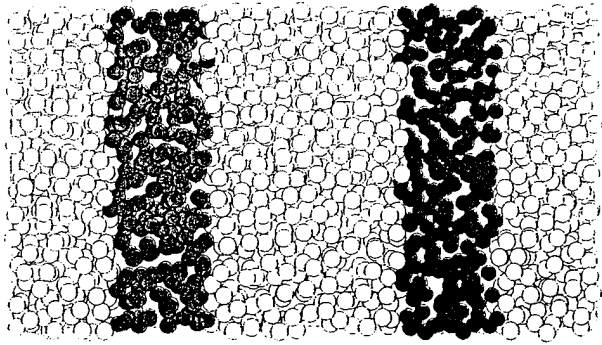


Fig 2

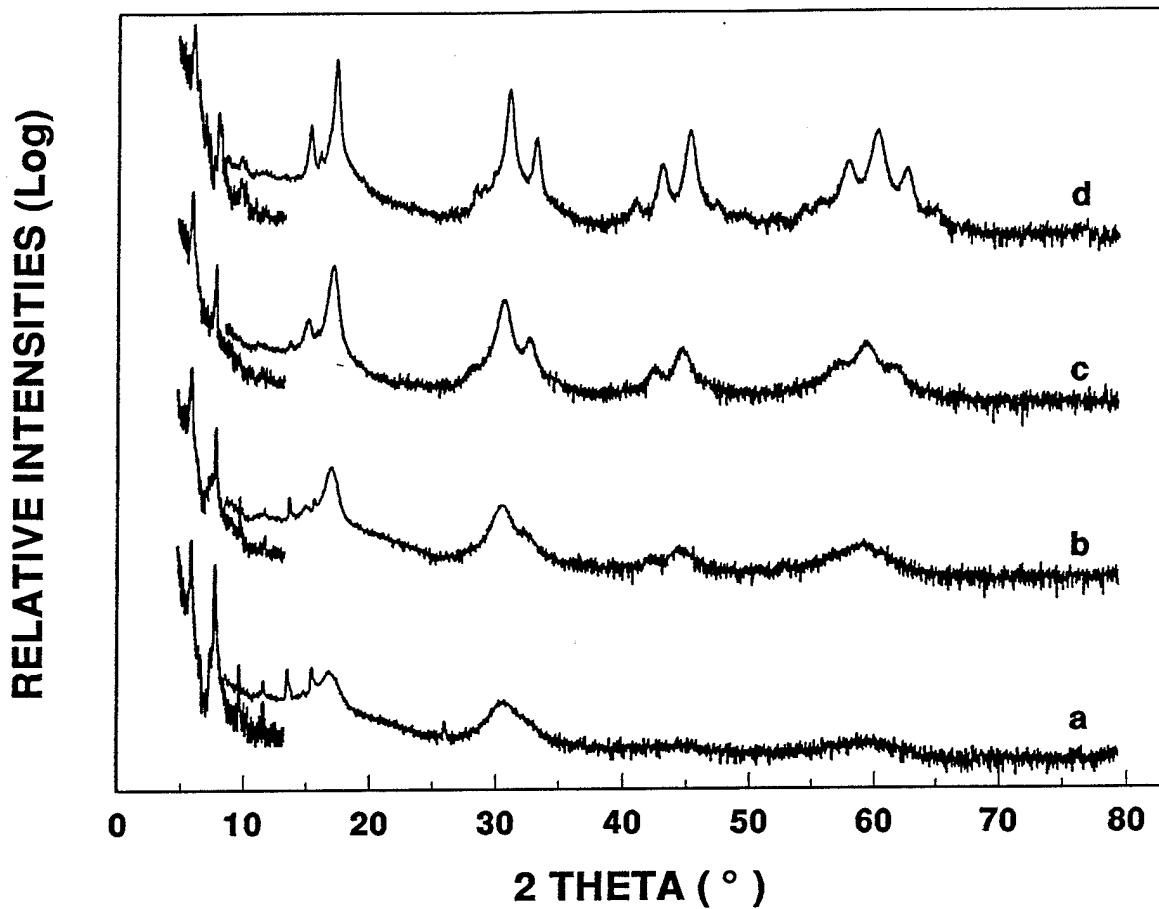


Fig. 3

$$\Lambda = 43.472 \pm 0.015$$

3.5 Ni:Se₃ / 3.5 Ti:Se₃ superlattice

a : Ag-deposited

b : 2H at 200°C

c : 2H at 350°C

d : 2H at 500°C

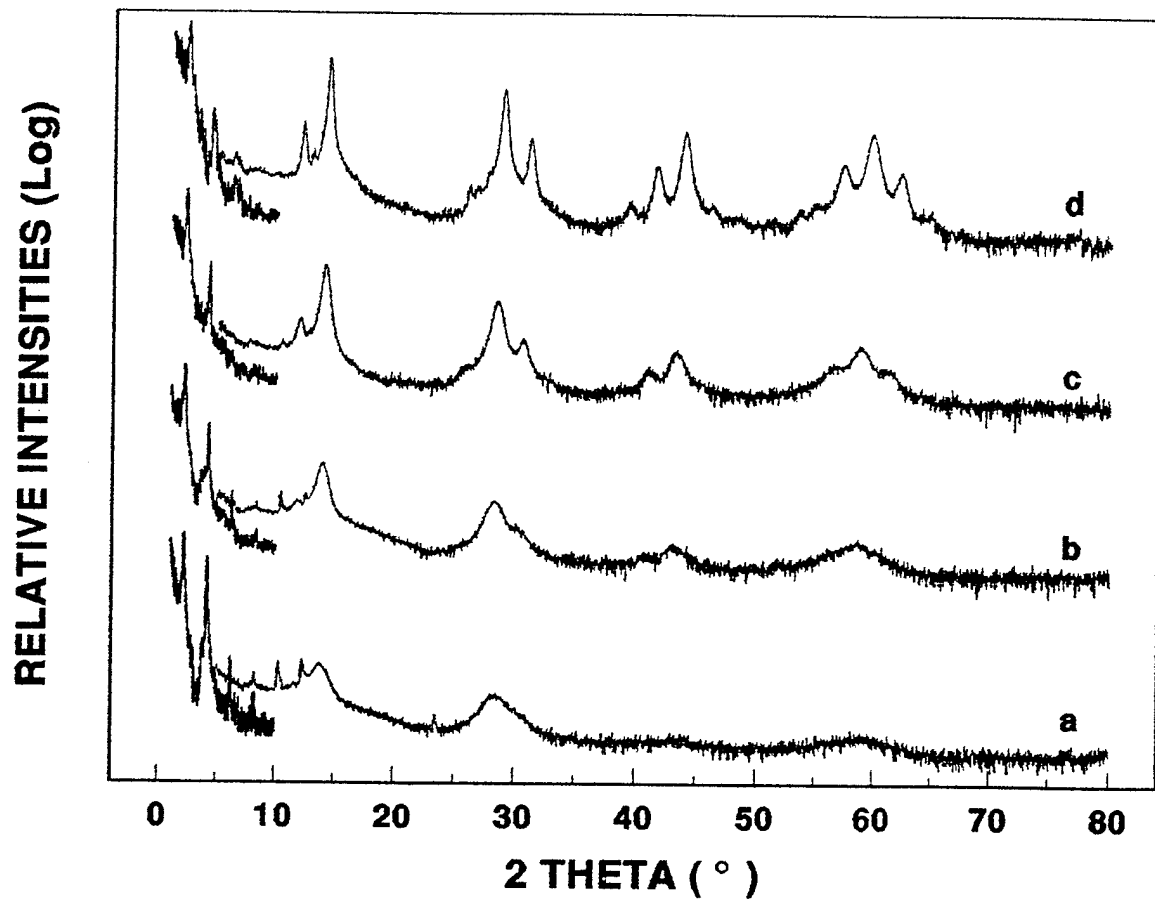


Fig 4

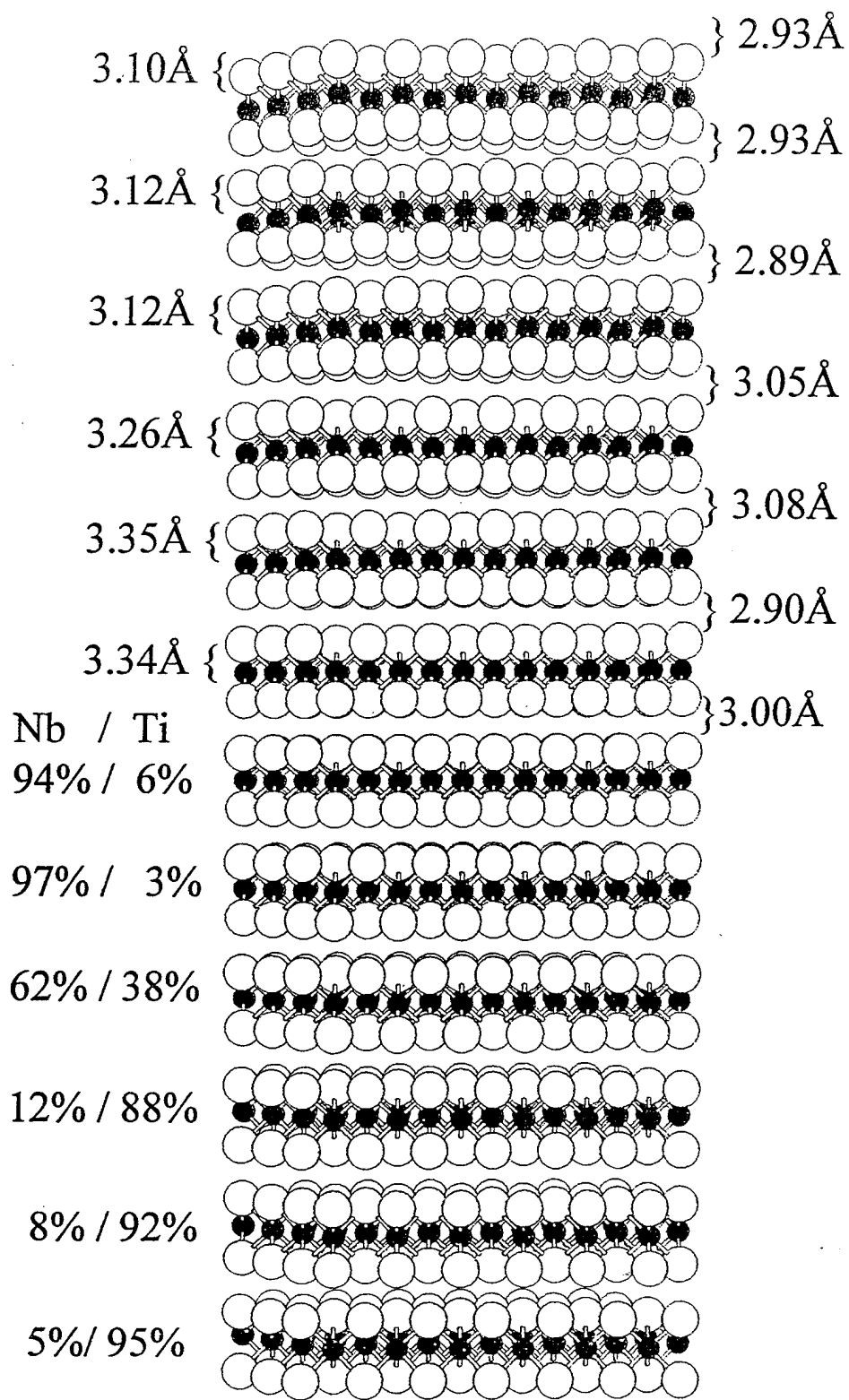


Fig 5