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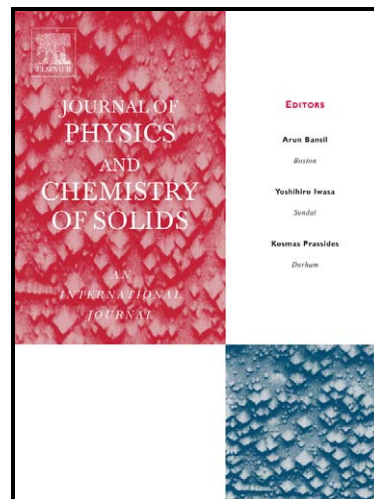
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A mesoscopic model of the intermixing during nanoenergetic materials processing

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Abstract

A general mesoscopic model for the simulation of thin film vapor deposition applied to energetic materials, specifically bimetallic multilayers, is presented. We describe the set up of this mesoscopic simulator developed in the frame of a multiscale study by implementing *ab initio* data into a set of differential equations. We present numerical results relative to the formation of barrier layers as a result of interdiffusion between successive bimetallic AlNi multilayers. The key role of the vacancies species created during deposition is highlighted.

1. Introduction

Nanostructured reactive multilayer films are typically formed by alternating chemically distinct materials [1-9] such as Al/Ni, which release heat during mixing. With the thin film vapor deposition techniques, such as Physical Vapor Deposition (PVD) [4,6,10] or Atomic Layer Deposition (ALD) [11], intimate and nearly perfect layers can be processed leading to highly reactive materials [12].

The performances of these energetic materials in terms of stability and reactivity are dependent on the composition, atomic structure, thickness and intimacy of the nanoscale layers. During deposition processes, atomic migrations give rise to an interfacial premixing layer between the two pure polycrystalline constituents [5]. This intermixed layer, in which both composition and structure are unknown, is shown to be one of the major sources of the overall loss of performance of the energetic materials. For instance, it is shown that the intermixing region has a major impact on the thermodynamic driving potential such as the degradation of the self propagating reactions and the reduction of the stored chemical energy [5,10,13,14]. Controlling this interface structure and its formation become crucial in order to get tailored energetic materials in terms of ignition rate and amount of released energy. Our aim in this work is to investigate how the formation of the intermixing layer can be shaped by adjusting the parameters of the deposition process.

In the following, we describe a novel mesoscopic modeling frame in which multilayer deposition is achieved allowing explicit treatment of exothermic reaction with associated dissipation and combustion phenomena. In more details, this mesoscopic model has three main characteristics which make it apart from the other existing models. First, the interfacial layer is not “*hand-built*” but is formed during the simulation of the deposition process. This simulator could thus be used as a pre-calculation step for a global multi-scale simulation procedure. The objective is to guide other existing approaches [15,16] of the combustion

process based on artificial “*hand-built*” premixing layer, in order to get a more representative interfacial premixing zone. Second, this model is set up by considering a bottom-up approach [17,18] where *ab initio* calculations are performed in order to characterize the elementary atomic scale mechanisms (structurally and energetically) occurring during the deposition process. These mechanisms are then used as input parameters in our mesoscopic model. In this manner, the model does not rely on adjustable nor empirical parameters and is only based on theoretical considerations. For sake of brevity, the *ab initio* data will not be discussed in the present paper. Third, the model is original because it includes mechanisms which are environment dependent with a meso/macroscale model: each atomic reaction is driven by the local composition of the layer in which it occurs. This predictive model is able to establish a direct link between the species concentrations in each layer of the material and their relation with the composition of other layers and the processing parameters. Although the model is generic for bilayer materials, we detail, in this paper, a set of equations intended to be validated on the model system composed of a bimetallic material, i.e. an AlNi multilayer film.

2. Methodology: Mesoscopic modeling

2.1 Atomic scale mechanisms

Using *ab initio* calculations, we have identified eight general elementary reactions that can occur in the multilayered Al/Ni materials: three of them are described as *intra-layer* reactions and the five others are *inter-layer* reactions. On the other hand, these reactions are qualified as: (i) “creation” like a defect formation mechanism, (ii) “exchange” between two chemically distinct atoms and (iii) “diffusion” mechanisms through the layers. We denote respectively as SAl and SNi, aluminum and nickel atoms positioned on a lattice site of the *fcc* crystals; as IAl and INi, aluminum and nickel atoms in a non-lattice position, and as V a vacancy. This vacancy can be initially present in the layer, created by atomic migration between the layers or provided to the system during the deposition process.

We detail in the following the *intra-layer* reactions occurring in a layer referred to as n , and *inter-layer* reactions occurring between two adjacent layers referred to as n and $n \pm 1$. These elementary mechanisms are written as:

- Vacancy formation [19,20], providing a vacancy (V) and a non-lattice atoms (IAI or INi) [21] from an atom in a lattice position (SAI or SNI), is considered for both constituents:



This reaction is considered as possible in the model despite its large formation energy for Ni-Al system, estimated at roughly 8 eV using *ab initio* calculations, since the model is generic and does not refer to this special case. The occurrence of this reaction is however automatically inhibited in Ni-Al system because of its very low reaction rate.

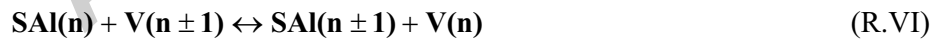
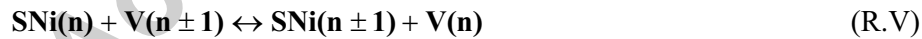
- Exchange between two kinds of chemically different species, respectively in lattice and non-lattice positions



- Exchange of two crystalline species present in two adjacent layers is allowed:



- Two diffusion mechanisms mediated by the presence of a vacancy



- Two mechanisms relative to the diffusion of non-lattice species



These reactions have been characterized using *ab initio*/Density Functional Theory. Five different systems have been considered. Two are pure Al and Ni bulk materials, one is AlNi bulk alloy and the two remaining represent Al(111) and Ni(111) surfaces. Each system consists of a supercell of 96 atoms distributed in 6 layers of 16 atoms. Periodic boundary conditions are applied in all three directions. These results are still the subject of current research and should be published soon.

2.2 Implementation of the Chemical Rate theory

In order to access to the temporal evolution of the system during the technological process, it is necessary to follow the concentration of each species constituting the layer. The species concentrations are noted as [S_{Ni}], [S_{Al}], [I_{Ni}], [I_{Al}] and [V] for the five identified species.

Two kinds of mechanisms have been distinguished:

- The “incoming molecular flux” providing species during deposition and filling in the empty layers. *Ab initio* calculations have shown that both atomic adsorptions of Ni on Al(111) and Al on Ni(111) result in hexagonal lattice positions S_{Ni} and S_{Al}. The adsorbed atom is placed above adjacent sub-layer bulk lattice atom. The incoming molecular flux is distributed among successive deposited layers, proportionally to the area exhibited by each layer. The adsorption mechanism which does not require any activation energy is driven by the Maxwell Boltzmann statistics in the gas phase, expressed as:

$$\Phi_{\text{gas}} = C \frac{P_{\text{gas}} S}{\sqrt{M_{\text{gas}} T_{\text{gas}}}}$$

with P_{gas} the partial pressure of the considered gas (Pa), S the surface of the elementary cell (considering Al or Ni lattice parameter) (m^2), M_{gas} the molar mass of the gas ($\text{kg}\cdot\text{mol}^{-1}$), T_{gas} the gas temperature (K), and C a constant. In this manner, the pressure and the temperature of the incoming gas are introduced as in a real processing experiment.

- For all others implemented mechanisms, the performed *ab initio* calculations reveal that an activation energy is required. This energetic barrier determines the probability of occurrence of a given event that depends also on the temperature. This is implemented in the model using the Arrhenius law which leads to the reaction constants \mathbf{k}_i :

$$\mathbf{k}_i = \mathbf{v} \times \mathbf{e}^{\frac{-A_i}{R_g T_{\text{layer}}}}$$

With A_i the activation energy of the mechanism i ($\text{J}\cdot\text{mol}^{-1}$), R_g the ideal gas constant ($8.31 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) and T_{layer} the time dependent layer temperature (K). \mathbf{v} is a dynamic prefactor corresponding to the Debye frequency. \mathbf{v} represents an attempt frequency of jump and is estimated at 10^{13} s^{-1} .

The effects of phase changes in the film such as alloy formation due to the melting of the reactants or products formation are neglected.

2.3 Implementation of heat exchange

The chemical reactions occurring in the energetic materials are highly exothermic and produce heat during mixing. This heat release is also present during the deposition process due to atomic migration leading to a structural rearrangement and to the formation of the premixing zone. In order to build a realistic and accurate model dedicated to the energetic materials, the temperature variations in the multilayer films have to be taken into account. We assume a uniform time dependent temperature throughout the multilayer film. This approximation is mainly justified by the small thickness of the multilayer films, of the order of few nm, compared to the thickness of the silicon substrate, of the order of $100 \mu\text{m}$. Spatial variations of the temperature, if present, occur only in the silicon substrate. They could be taken into account via heat conduction in the silicon substrate film. However, these spatial

variations are not implemented in this first version of the model, since we consider only mechanisms where the atomic species diffusivities are smaller than diffusivity. In this model, temperature variations result from exothermic reactions and the convective and radiative heat losses on the wafer surfaces. Concerning the radiative heat losses, the multilayer film is approximated as a black-body radiating with unit emissivity, which ideally exchanges with unbounded surroundings at ambient temperature.

Also, in the present version of the model, physical properties such as thermal conductivity, density and heat capacity are assumed to be independent of the temperature and of the layer composition. In a future version of the model, the temperature dependence of these parameters can be easily taken into account, if necessary. Considering the above points, the temporal evolution of the temperature can be written as:

$$\rho_{\text{Si}} c_{\text{Si}} e_{\text{Si}} \frac{dT}{dt} = \sum_i Q_i - h(T - T_0) - \sigma(T^4 - T_0^4)$$

With ρ_{Si} the silicon density (2330 kg.m^{-3}), c_{Si} the silicon heat capacity ($700 \text{ J.kg}^{-1}.\text{K}^{-1}$), h the convective heat exchange coefficient, e_{Si} the silicon substrate thickness (m), T_{Si} is the temperature of the silicon substrate, σ the Stefan-Boltzmann's constant ($5.67 \times 10^{-8} \text{ W.m}^{-2}.\text{K}^{-4}$), T_0 the ambient temperature and Q_i the heat released by each exothermic reaction during the time interval dt . This last parameter is environment dependent (Section 2.4).

The model is therefore composed of $5n + 1$ differential equations for the description of the concentration variations for a material with n layers: five equations for the five species in each layer and one equation for the uniform temperature.

2.4 Implementation of the environment dependent reactions

The originality of the model is that the activation barriers A_i are environment dependent: they explicitly depend on the composition of each layer and account for the heat production

noted as Q_i . In order to implement this environmental dependence in the model, the total energy is assumed to be the sum of an electronic term and nearest neighbor pair interactions.

The energy of an atom of type J can then be written as:

$$E(\mathbf{J}) = E_0(\mathbf{J}) + n_j \varepsilon_{jj} + n_k \varepsilon_{jk}$$

Where E_0 corresponds to the electronic term, n_j and n_k are the ratios of species j and k in the layer, and ε_{jj} and ε_{jk} are the pair interaction energies between two nearest neighbors, of

the same type or of different types, respectively. The ratios n_j and n_k of species in the layer

$$\text{are expressed as } n_j = \frac{[J]}{[J] + [K] + [V]} \text{ and } n_k = \frac{[K]}{[J] + [K] + [V]}.$$

Where $[J]$, $[K]$ and $[V]$ respectively stand for the concentrations of J and K species, and for the vacancy concentration. We have assumed that vacancies may be present in the layers as a result of kinetic effects and the lattice mismatch between the two materials.

The energy values for the starting position, the final configuration and the transition state are evaluated at each step of the simulation, for all possible elementary reactions and for each layer in the film. Using these calculated energies (Figure 1), the activation energies A_i as well as the released heat Q_i for both the direct and the reverse reactions and for each elementary mechanism can be determined. In this way, the knowledge of only three energetic parameters dependent on the composition of each layer, allows us to address the desired environmental dependence.

3. Preliminary results

In the following, we present preliminary results concerning the Ni/Al multilayer bimetallic films deposited on silicon substrates. The aim of the simulation is a first validation of the model through a simple system for which experimental and theoretical data are available in the literature. Also, the technology process conditions have been simplified as much as

possible. For instance, the temperature has not only been considered as uniform over the whole sample, but also constant in time and equal to the ambient temperature. This approximation is justified in cases where the silicon substrate is strongly cooled during metal deposition.

In all following simulations, the ambient temperature is kept fixed at 298 K. The incoming gas is at 350 K under a pressure of 0.005 Pa. We mainly focus on the role of vacancies present at the interface between the two nanolayers. Our objective is to understand to what extent their presence is necessary for the formation of an intermixed zone between the pure nanolayers. In a first set of simulation runs, we successively investigate the deposition of Ni/perfect Al(111) substrates and of Al/ perfect Ni(111) substrates, to get insight on both interfaces. However, in these preliminary simulations, we have not examined multilayer deposition. All simulations of this set run for 3s with $e_{\text{Si}} = 1 \mu\text{m}$.

The atomic pair interaction energies have been estimated via *ab initio* calculations. Five periodic structures of pure Al, of pure Ni and of AlNi alloy have been considered using a large spectrum of situations: vacancies, interstitials, Frenkel pairs, atom/surface interactions...

The values for the electronic energies and the pair interaction energies have been estimated by fitting the total energies to the corresponding values obtained using DFT, in all considered cases. The best fit is observed for: $E_0(\text{Ni}) = -3.4155 \text{ eV}$, $E_0(\text{Al}) = -2.8533 \text{ eV}$,

$$\begin{aligned} \epsilon_{\text{SNI-SNi}} = -0.5225 \text{ eV}, \quad \epsilon_{\text{SAI-SAl}} = -0.2214 \text{ eV}, \quad \epsilon_{\text{SAI-SNi}} = -0.7452 \text{ eV}, \quad \epsilon_{\text{INi-SNi}} = -0.2191 \text{ eV}, \\ \epsilon_{\text{INi-SAl}} = -0.5695 \text{ eV}, \quad \epsilon_{\text{IAI-SAl}} = -0.0507 \text{ eV} \quad \text{and} \quad \epsilon_{\text{IAI-SNi}} = -0.1981 \text{ eV}. \end{aligned}$$

Interactions between two non-lattice positions (INi-INi, IAl-IAl, IAl-INi) have not been considered in this first version of the model, due to the low probability of finding two interstitials close to each other.

For both cases, deposition of Ni or Al, we consider that the first material is already deposited so that the starting point of the simulation concerns the deposition of the second material.

Figure 2a represents a schematic view of the starting configuration and the partially covered

layers during the process. Figure 2b shows the actual coverage of the successive deposited layers versus time. No vacancy supply has been introduced in this first set of simulations. At the end of the simulation, the compositions of the deposited layers and of the substrate layers are very close to the pure constituents. This reveals that during the deposition of Al/Ni(111) or Ni/Al(111), with a growing multilayer film maintained at ambient temperature, no interfacial mixing can be obtained if no vacancy is provided during the deposition process. In fact, the considered atomic scale reactions are very difficult to occur in these metallic materials at low temperatures, as expected from DFT results.

For instance, if we focus on the exchange between two atoms, S_{Ni} or S_{Al}, described in the reaction R.IV, the exchange of S_{Ni} located in a pure nickel layer with a S_{Al} located in a pure aluminum layer, will require energy barriers up to 5 eV. This has been determined using *ab initio* calculations where the theoretical minimum energy pathway is characterized by a multi-step reaction involving several non-lattice positions for the migrating species and its neighboring atoms.

Despite the small intermixing occurring during room temperature simulations, we can still observe two general trends, in agreement with *ab initio* calculations performed to determine the adsorption pathways. The first concerns the heat loss during deposition which is larger when Al is deposited on a Ni substrate. The second is that the intermixing is asymmetric: Ni atoms penetrate easily the Al(111) substrate, while Al remains on Ni(111) surface. The theoretical pathways obtained show that only a 0.06 eV activation barrier allows the penetration of the Ni atom into the first Al(111) sub-layer. The activation barrier for the migration of the Ni atom into the second Al(111) sub-layer is of 1.2 eV, in the range of bulk migration energies. Looking at the Al on Ni(111) case, the activation barrier for the Al atom to penetrate the first Ni(111) sub-layer amounts to 1.56 eV, much higher than the previous value. This reaction is practically forbidden at room temperature. Therefore, the intermixed zone, for room temperature processes, results at the Ni/Al(111) interface rather than at the

Al/Ni(111) interface. This asymmetry shows that tuning experimental conditions is a key for the optimization of the multilayer films, particularly in terms of formation of intermixed zones. These conditions might eventually be different for the two, Ni and Al, deposition processes.

In a second set of runs, the simulations are performed by considering a perfect material composed of four Ni monolayers in direct contact with four Al monolayers and a film temperature maintained at 298 K. These simulations run last for 1s with no incoming gas flux. When an artificial amount of vacancies, 10 % here, is introduced in the interfacial monolayer between the two pure constituents, the mixing reactions are activated, even at room temperature. Here, we wish to emphasize that the vacancy presence in the interfacial layer will be key in the mixing taking place during the vapor deposition as the vacancies favor the mixing at the interface. Indeed, activation barriers, as calculated using the three states (Figure 1), are strongly reduced in the presence of vacancies.

4. Conclusion

During multilayer deposition processes, an intermixing reaction inevitably occurs between the two constituents leading to the formation of a premixed zone which separates pure layers of the films. This paper presents a first attempt to set up a model for the deposition process and the structural arrangement during the deposition, based on a multi-scale approach combining chemical rate theory and *ab initio* results. In these preliminary results, a first trend appears: the diffusion of Ni species seems to be easier across the bulk compared to the Al species diffusion. The key role of vacancies species provided to the system during the deposition process is also highlighted. We reveal that if no vacancy supply is provided during deposition process, for multilayer films maintained at ambient temperature, it is tricky to form an interfacial premixing layer due to the high activation barriers required to allow atomic reactions. We have shown that, in order to develop a realistic model of the deposition process,

it is necessary to investigate and implement the mechanisms of supply of vacancies to the interfacial region. As a result of the preliminary results discussed in this paper, future work includes an accurate and realistic rate of vacancies supply during deposition process. Beyond these developments, the model presented here could be coupled to other existing modeling approaches as they mainly focus on the heat loss phenomena due to the intermixing layer, or on the combustion process. These models, starting usually from empirical premixed layers, can use our approach to define process dependent initial configurations.

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Figures caption

Figure 1: Schematic view of an elementary chemical reaction exhibiting the three energy levels: E_I , E_F and E_T , used for the calculation of thermodynamic (Q) and kinetic (A) parameters.

Figure 2: (a) Schematic views of the starting configurations of the multilayer films before deposition (left) and during deposition (right), (b) Evolution of the successive layers coverage versus time.

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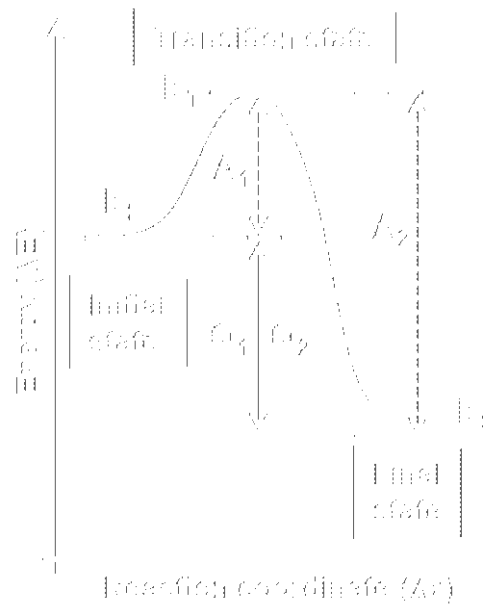


Figure 1

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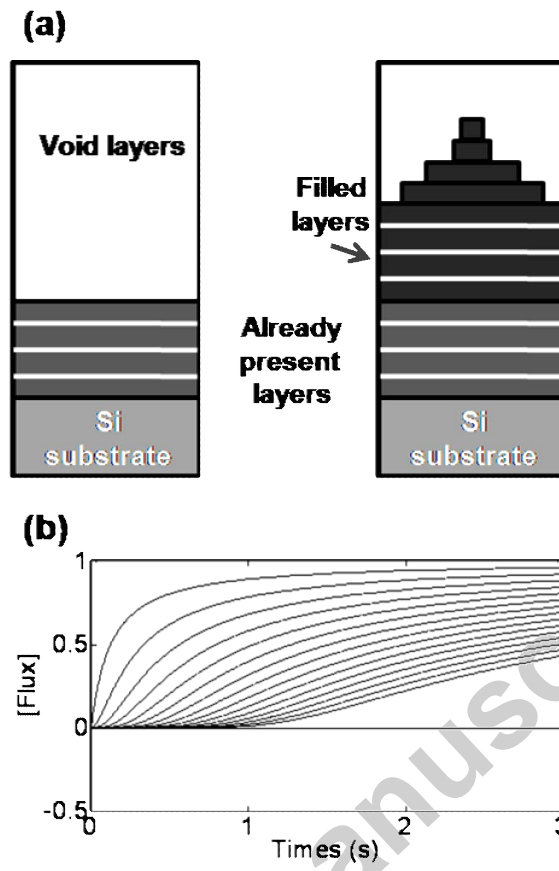
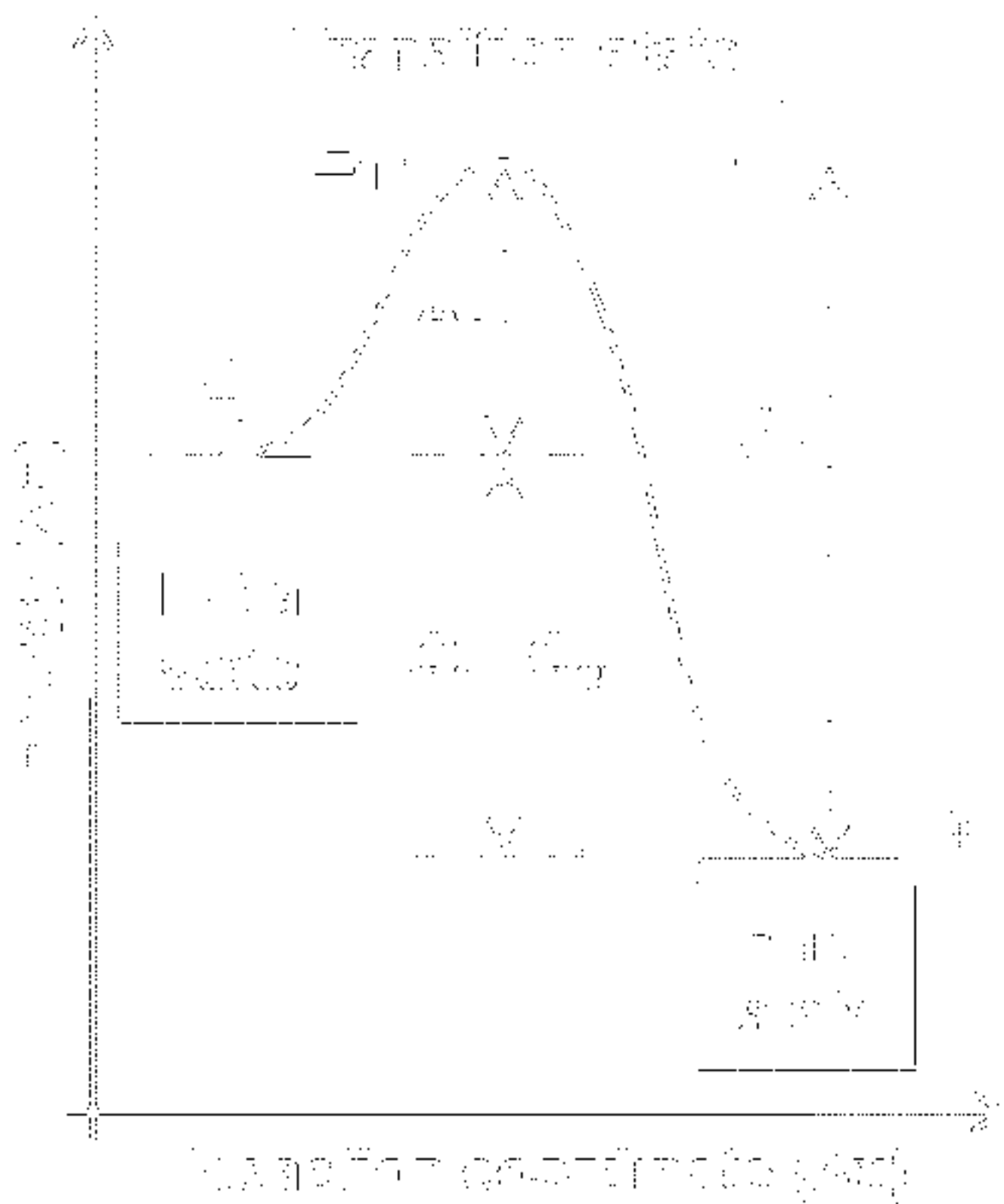
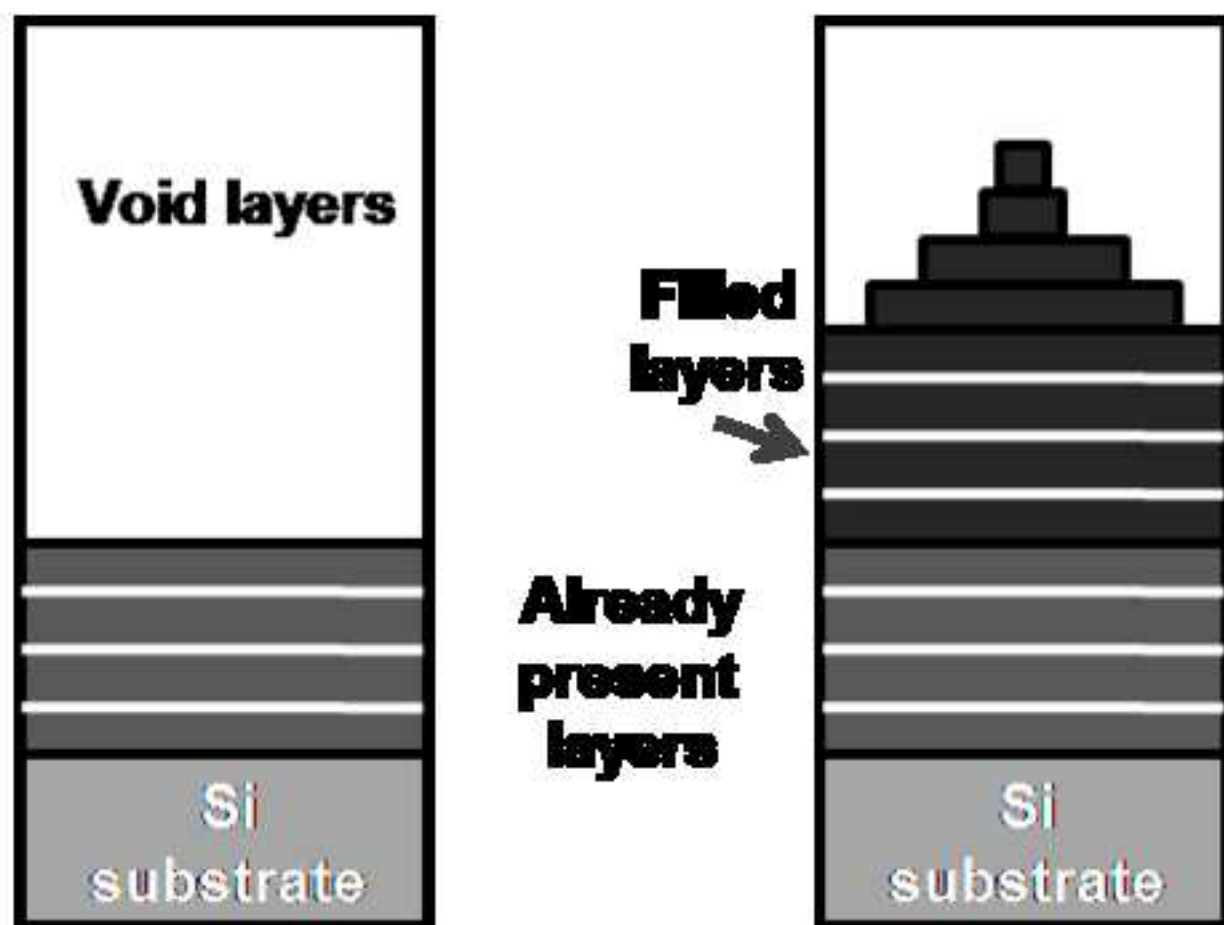


Figure 2



(a)**(b)**