SYNTHESIS OF METASTABLE BULK AND EPITAXIAL PHASES

Raymond Kern

C.R.M.C^2 - C.N.R.S., Campus de Luminy, Case 913, 13288 Marseille, Cedex 9 France

Abstract - Metastable solid phases are defined as unstable phases transforming so slowly that they seem stable. A metastability time τ is defined from nucleation theory and some examples are considered from the point of view of Buerger's phase transition classification. Addition of some dopants may act as stabilizers or, in contrary, as destabilizers. How to synthetize metastable phases may be important to know in order to produce new solid materials. This is a game of kinetics of production and kinetics of disappearance. Substrates may initiate the nucleation of metastable phases when there is some favorable epitaxial relationship.

INTRODUCTION

A phase which is characterized by its composition, structure and form is called stable when it occupies a domain $D(P,T,n_i)$ in the equilibrium phase diagramm of the system, system meaning the phase itself plus the mother phase. For practical use of such a phase there is an other domain $D_0(P_0, T_0, n_{oi})$ where P_0, T_0 are usually normal pressure and temperature, n_{oi} vacuum or air. When there is some intersection of D and D_0 the phase can be used in its stable state. If not, it is unstable and looses its practical interest. Fortunately, very often, there is metastability and such an unstable phase can be used for more or less long time. The phase is internaly frozen, it transforms so slowly that its user ignores that it is transforming. Fortunately diamond is strongly metastable. The same is true for glass, amorphous semiconductors and so on. To have at our disposal metastable phases increases the number of practical applications for new materials produced in the laboratory. These possibilities are enhanced when metastable phases can be produced which have no stability domain at all. The production of such phases is called metastable synthesis.

METASTABILITY TIME SCALE τ

What are the parameters characterizing the time scale τ of a metastable phase, labelled II, when transforming in the stable phase, say I ? τ ranges from billions of years for the diamond-graphite transition to milliseconds for the $\alpha \rightarrow \beta$ transition of sulphur.

Clearly it is not the heat of transition ΔH(II-I) which can tell something about τ since all heats of polymorphic transitions are of the same order and small. Inside phase II the molecules have to displace at short distance, bonds must eventually be broken, what can be summarized by an activation energy A_D(II-I). These species have to reorganize, form nuclei of the new phase I, what we summarize by nucleation activation barrier A_N(II-I). The measure of τ may be then from Volmer's nucleation theory (Ref. 1)

$$(1) \qquad \tau \propto \left[1 - \exp(-\Delta\mu(II - I)/kT)\right]^{-1} \exp[A_N(II-I) + A_D(II-I)]/kT$$

A_D (II-I) is some kind of "molecular viscosity" temperature coefficient, viscosity which may vary strongly with temperature. The nucleation barrier

$$(2) \qquad A_N(II-I) = c(I)\sigma^3(II-I)/\Delta\mu^2(II-I)$$

TABLE 1.   Kinetic characteristics of some phase transitions.

Reconstructive		$A_D(II\text{-}I) > 0$ kcal.mole^{-1}	$A_N > 0$ $\sigma(II\text{-}I)$erg cm^{-2}	
First coord.	Diamond → graphite	60	3 000	high metast.
	$As_4O_6 \rightarrow (AsO_{3/2})oo$	40	500	"
Change	$\mu - S \rightarrow \alpha - S$	50	200	"
Second coord.	Co(FCC) → Hex	50	20	metast.
	Ni(Hex) → FCC	50	150	"
Change	ZnS(Hex) → Cubic	20	600	"
	$\beta - S \rightarrow \alpha - S$	10	18	small
Non Reconstructive		$A_D(II\text{-}I) > 0$ kcal.mole^{-1}	$A_N \sim 0$ $\sigma(II\text{-}I)$erg cm^{-2}	
Substitutional	Si,Al Feldspars	50	~ 1	metast.
	Fe,Mg Olivines	40	~ 1	"
Displacive	$\beta SiO_2 \rightarrow \alpha SiO_2$	3 - 5	2	no metast.
Rotational	CI_4 , CH_4	< 1	~ 0	no
	Magnetic domains	~ 0	$\sim 5 - 10$	metast.

is characterized by the interfacial tension $\sigma(II\text{-}I)$ of the two phases in contact, a form factor $C(I)$ of the newly created nuclei and especially by the thermodynamic "driving force", or affinity, which in the most simple case is only the degree of overpassing equilibrium

$$(3) \qquad \Delta\mu(II\text{-}I) \simeq -\Delta H(II\text{-}I)\left[1-T/T(II\text{-}I)\right]$$

$T(II\text{-}I)$ is the coexistence temperature of both phases, T the actual temperature.

Buerger's (ref. 2) crystal chemistry classification of phase transitions helps much to have a qualitative look on the time scale τ. For reconstructive transitions the new phase has to be rebuilt with fragments of the old one so that nucleation is a necessity, $A_N \neq 0$ and the interfacial tension $\sigma(II\text{-}I)$ may be high due to a strong discontinuity at the interface. When for this type of transitions $A_D(II\text{-}I)$ is further more high, e.g. strong first coordination bonds in phase II having to be broken, then the transformation is very sluggish. Examples are diamond graphite, claudetite - arsenolithe, polymeric μ - sulphur to S_8 sulphur. In contrary A_D (II-I) may be smaller when only second coordination changes has to occur as in FCC cobalt to Hex cobalt, or Hex Ni to FCC Ni, or β sulphur to α sulphur. A_D (II-I) has then the meaning of an hole formation-migration activation energy.

For non-reconstructive transitions $A_N \simeq 0$, since there is a quasi continuity of structure across the interface and therefore $\sigma(II\text{-}I)$ is small. The time scale τ is thus reduced. This is particularly true for displacive transitions or rotational transitions for which there is also $A_D(II\text{-}I) \simeq 0$. Often these transitions behave as reversible, e.g. all α-β transitions for SiO_2, those of the so called plastic crystals, or magnetic transitions. Much more sluggish are the order-disorder transitions of substitutional type since $A_D(II\text{-}I)$ may be high, e.g. the Si, AL order-disorder in feldspars. Table 1 gives, by following Buerger's classification , the values of $A_D(II\text{-}I)$ and $\sigma(II\text{-}I)$ intervening in A_N for some typical examples.

STABILIZERS AND DESTABILIZERS

Some dopants or agents can act on the metastability. The best stabilizing agent may be temperature when the maximum value of the nucleation frequency $1/\tau$ can to be overpassed toward the lower temperatures. (Plot $1/\tau$ versus T according (1) (2) (3) and observe that the maximum is thus more located at high T than $A_D(II\text{-}I)$ is high). When this is not quite possible then low temperature does not help what is the case when $A_D(II\text{-}I)$ is small. Stabilizing substances are well known and called glass forming elements, for SiO_2 and also metals, substitutional or intersticial elements increasing the bond strength thus $A_D(II\text{-}I)$. Amorphous silicon is stabilized by hydrogen which saturates some dangling bonds. Polymeric μ - sulphur is stabilized by saturating the chain extremities with the help of substances giving free radicals. The polymorphs of NH_4NO_3 are stabilized by mixing them with some salts which have structural analogies with phase II so that there is probably some epitaxial stabilization (Ref. 3).

Destabilizers are well known also. They decrease $A_D(II\text{-}I)$ so that the time scale τ drops.

For glass they are called "mineralizers", that can be sodium or potassium weakering the Si-O skeleton and lowering the "melting temperature" (see above T as stabilizer). But also water vapour lowers $A_D(II\text{-}I)$ by helping to cut Si-O bonds of the skeleton, initiating therefore the crystallization of the glass from the surface to the bulk. Polymeric μ - sulphur is very sensitive to H_2O, H_2S, NH_3, these species cutting easily the sulphur chains so that S_8 molecules form more easily giving the α - sulphur.

Physical agents may act also as destabilizers by damaging the metastable phase. Surface scratching, plastic deformation, inhomogeneous cooling help, as mechanical agents, to breake bonds or to favour local diffusion. Amorphization by fast particles as electron, or heavier ones by recoil effect, may reduce $A_D(II\text{-}I)$. Light irradiation may play in the same sense, ions may be created acting as nucleation centers lowering then $A_N(II\text{-}I)$ also.

METASTABLE SYNTHESIS

The metastability of phase X having been recognized, how to produce it from a mother phase m ? Ostwald's "step rule" stipulates that the sequence of appearence of phases, X, Y, ... goes in the sense of increasing energy content of these phases. Fortunately, Ostwald's rule suffers many exceptions. Without such exceptions metastable synthesis would not be possible. Stranski (Ref. 4) discussed Ostwald's rule in context of Wolmer's nucleation theory. He showed that among the phases I, II, ... X ... appears first this one whose activation energy of formation $| A_D(m\text{-}X) + A_N(m\text{-}X) |$ is the smallest. One has to play with the first, the second term or with both.

In the case of the metals Ni and Co the hexagonal phase can be obtained first at high $\Delta\mu$ values, since the form factor in relation (2) is approximately four times smaller for the hexagonal nuclei than for the cubic ones, so that in spite of similar surface tension values of both phases, the hexagonal phase is largely favoured.

Polymeric μ - sulphur can hardly be obtained from sulphur vapour containing only S_8 molecules since the A_D term is too much high. But at high temperature the S_8 molecules can be predissociated so that the A_D term does not play any longer.

An other good example is the claudetite phase and the arsenolithe phase, both polymorphs of As_2O_3. From the vapour phase containing closed As_4O_6 molecules only arsenolithe crystals can be deposited, these crystals containing the same As_4O_6 molecules loosely bond by Van der Walls bonds. In order to deposit at the same temperature claudetite crystals, the vapour has to be predissociated by passing over a hot filament. Claudetite crystals have an ionic structure of $(AsO_{3/2})$ building units so that the As_4O_6 molecules have first to be cut in pieces before they can rearrange as a ionic crystal. Chemical agents as HCl may help in similar way.

SUBSTRATE EFFECTS (Ref. 5, 6)

Great advantage can be obtained for metastable synthesis by using a foreign substrate. The nucleation barrier A_N (called also homogeneous nucleation barrier), is lowered by the presence of any surface (wall effect) to $A_{N,s}$. The generalized Wulf's theorem by Kaishew tells that :
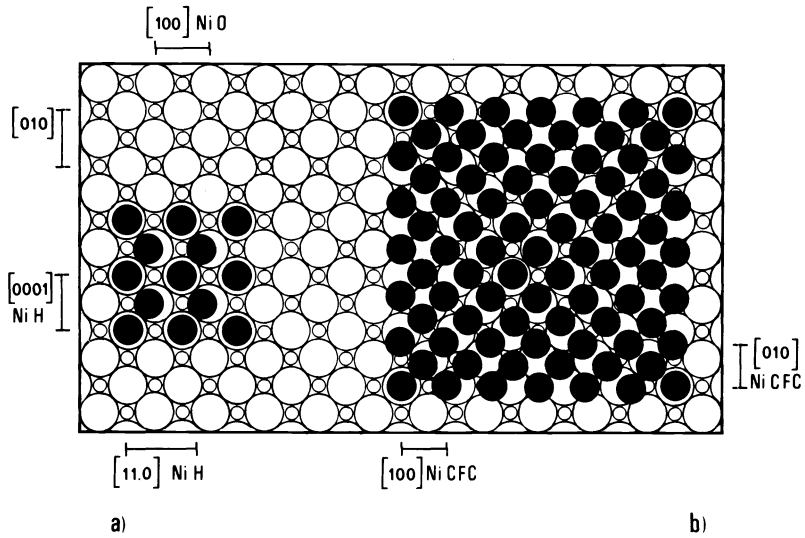
Fig. 1. NiO cleavage (100) face

    In a), hexagonal nickel monolayer lying with a (11$\bar{2}$0) face on NiO (100).
        The misfits are small : Ni $|0001|$ // NiO $|001|$ + 2 %
                              Ni $|11.0|$ // NiO $|010|$ - 3,5 %

    In b), FCC nickel monolayer lying with a (100) face on NiO (100) has a very
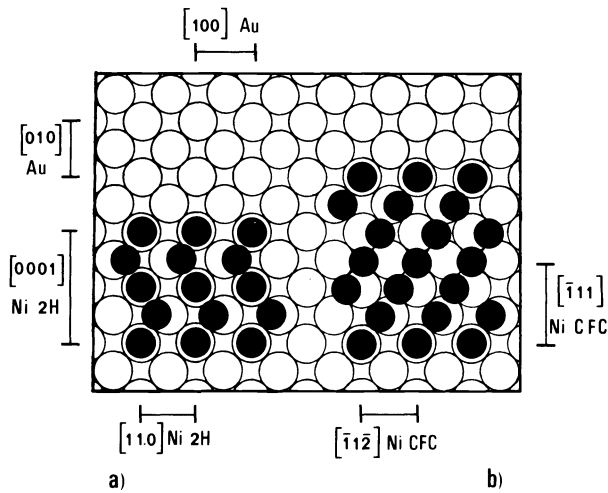   high misfit NiO $|001|$// Ni $|001|$ + 16 %.

Fig. 2. (100) surface of Au

    In a) a monolayer of hexagonal nickel is lying with a (11$\bar{2}$0) plane on
        (100) Au. It is the 2H polytype of nickel. The misfits are respec-
        tively + 5 % and - 6 % respectively in the vertical and horizontal
        directions.

    In b) a monolayer of FCC nickel is lying with its (110) plane on (001) Au.
        This corresponds to a deposit made at 350°C. The misfits in the ver-
        tical and horizontal directions are + 5 % and - 6 %.

$$(4) \qquad A_{N,S} = A_N[1-\beta(i,s)/2\sigma(i)]$$

$\sigma(i)$ is the interfacial tension of the new phase and especially in that crystallographic direction i with which this phase will later be in contact with the substrate s. β (i,s) is the adhesion free energy of the new phase with the substrate in precise orientation (i,s). β (i,s) is the higher the stronger bonds are established between the deposit and the substrate. Further more when substrate and deposit are crystalline an epitaxial misfit decreases β (i,s), the highest value being for misfit zero.

When β (i,s) = 0 the substrate doesnt play any promoting role for nucleation but has the greated efficiency when β (i,s) = 2 $\sigma(i)$ since from (4) there is no more activation barrier for nucleation. (A two dimensional nucleation however persists in latter case, the corresponding barrier is however small).

When in a system several phases can be formed, that phase having the smallest $\beta(i,s)/2\sigma(i)$ ratio will nucleate first. The substrate has some phase selection power. Therefore it is possible to choice the substrate so that the wanted metastable is favoured. Diamond is metastable at normal pressure but it can be synthetized at this pressure by cracking of hydrocarbons, provided that an appropriate substrate is present. Unfortunately the synthesis works only when this substrate is precesely diamond too.

Cubic NaBr is metastable in a water solution when $T < 50°C$, the hydrate NaBr, $2H_2O$ being stable. However, cubic NaBr can be nucleated and can grow (Ref.7) at $T < 50°C$ provided a (100) PbS cleavage faced tips in the solution. Cubic NaBr crystals grow epitaxialy on (100) PbS which is quite isomorphous with NaBr.

There can be also $\beta(i,s) > 2\sigma(i)$ for which case, relation (4) is no more valid since two-dimension (2D) nucleation and growth then (Ref.5) takes place. Each layer is a proper 2D phase and even inside a monolayer different 2D phases may exist. These 2D phases may be similar to the corresponding 3D phases or may be different. They can be stable or metastable.

There can be distinguished a form metastability and structural metastability.

When Cu is deposited on a (111) Ag plane at ordinary temperature there is a formation of successive (111) Cu FCC full 2D layers up to a fourth layer. At $T > 200°C$, 3D crystallites of Cu FCC are formed with their (111) face in contact with the silver substrate. Between these crystals there is the bare substrate. In the first case the 2D layers are form metastable since by heating up to 500°C these layers shrink and transform in the second case. It should be interesting to prepare such layers of high specific surface and more interesting to render them more metastable so that they stand at higher temperature. Foreign adsorption of gas on such layers render them more form stable since by the gas adsorption (i) is lowered and therefore the β (i,s)/2σ(i) ratio is increased.

Structural metastability has been called also pseudomorphism by Finch when it is initiated by the substrate. When Fe is cold deposited on Cu(100) there is formation of FCC iron layers. At 400°C, 3D FCC iron crystallites form. The growth of this metastable iron is due to the fact that the mismatch between (100) Cu and (100) Fe, FCC is small. Hexagonal Ni has no stability domain at all whatever P and T. We looked at its homogeneous nucleation in 4. Substrate effects may favour its formation. When a (100) NiO face is reduced by H_2 at $T < 230°C$, 2D Ni layers or 3D crystallites under strain (see Fig. 1) are growing (Ref. 7). When Ni is vacuum deposited on a (100) Au crystal (Ref. 8), there is also growth of hexagonal nickel with its (11$\bar{2}$0) plane (See Fig. 2). In both cases there is a very small misfit with these substrates. An interesting fact is that when (100) NiO is somewhat damaged before the hydrogen reduction, hexagonal nickel doesnt no more form. The substrate loosed its promoting effect.

REFERENCES

1. M. Volmer, Kinetic der Phasenbildung, Leipzig, (1939)
2. M.J. Buerger, in Phase Transformations in Solids, Wiley, p. 183, (1951).
3. R. Hocart, A. Mathieu Sicaud, in Disc. Faraday Soc. n° 5, p. 237, (1949).
4. I.N. Stranski, D. Totomanov, Z. Phys. Chem. A.163, p. 516 (1939).
5. R. Kern et al, in Current Topics in Materials Science, N.H. Ed. Kaldis, Vol.3, p.131-419 (1979)
6. R. Kern, in Interfacial Aspect of Phase Transformations, Reidel Publ. Co, Ed. by Mutaftschiev, p. 287-302, (1982)
7. J.M. Rickard et al., J. Micr. Spectr. Elect. 4, p. 95, (1979).
8. F. Hila et M. Gillet, J. Micr. Spectr. Elect. 4, p. 571, (1979).