

Design of novel nanocrystalline composite materials by means of plasma CVD

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Abstract: We discuss two examples of the application of non-isothermal plasma CVD for the design of novel nanocrystalline/amorphous composite materials. It is shown that the electronic and mechanical properties of the materials undergo dramatic change when the crystallite size decreases below 10 nm where the localization phenomena of charge carriers and phonons commence: The probability of the phonon assisted radiative recombination of the carriers increases resulting in an efficient photoluminescence from nanocrystalline silicon. The mechanical strength of nc-MeN_x/a-Si₃N₄ composites increases far above the values of the single components. In both cases, a small crystallite size of ≤ 2 nm, sharp interfaces free of dangling and weak bonds and an appropriate thickness of the amorphous matrix are needed. So far, only plasma CVD appears to be able to meet these stringent requirements.

1. Introduction

The properties of many materials undergo significant changes when the crystallite size reaches the range of a few nanometers. Because of their technological applications, such **"nanocrystalline materials"** are receiving increasing attention, and in some cases, are already being used in industrial products (e.g. high density magnetic memories). In this paper we shall briefly discuss two examples from our recent work.

Silicon dominates the microelectronics but, because of its indirect band gap, it cannot be used in optoelectronic devices such as light emitting diodes and others. However, as it has been shown recently, porous silicon (prepared by anodic etching of Si-wafers in an HF/ethanol/water solution) with a crystallite size of few nanometers shows an efficient photoluminescence [1-5]. The disadvantages of porous silicon are its brittleness, high porosity and a relatively poor control of the crystallite size.

Therefore our work concentrates on the preparation of compact films of **nanocrystalline light emitting silicon** by plasma CVD and posttreatment (oxidation of the grain boundaries and annealing in forming gas) [6-8]. The plasma CVD technique allows us to exactly control the crystallite size and the mechanical stress in the films [9-11] as well as the thickness of the grain boundaries which all determine the efficiency of the photoluminescence [8,12,13]. Moreover, the technique is compatible with the silicon technology. The preparation procedure will be outlined together with some optoelectronic properties of the nc-Si films. So far, the plasma CVD is the only technique which, due to its flexibility, allows us an independent and precise control of the crystallite size and of the thickness of the grain boundaries which are decisive for the optoelectronic properties of the material.

The strength of ductile materials is determined by the movement of dislocations and, therefore, it is orders of magnitude smaller than the theoretical value for a perfect crystal. The precipitation hardening, which is one of the most important techniques for strengthening of materials [14,15], is based on the pinning of dislocations within the crystallites and/or the grain boundaries of microcrystalline materials. The strength increases with decreasing crystallite size according to the Hall-Petch rule [16,17]. A further increase of the strength is achieved in nanometer thin epitaxial heterostructures (superlattices) consisting of a suitable combination of epitaxial layers of two different metals or metallic nitrides which avoids the movement of the dislocations through the interface [18]. **The concept of our novel superhard nanocrystalline composites** [19,20] is based on a similar principle but, unlike the superlattices which are difficult to prepare (for an excellent review see [21]), it offers a series of possible materials for practical applications. We shall present results on the preparation and characterization of thin films with a hardness of ≥ 5000 Vickers, a high elastic modulus and a high ratio of the elastic recovery to the permanent deformation. Plasma CVD allows us to control the crystallite size within the desirable range of 1 to 3 nm and the thickness of the amorphous matrix in which the crystallites are imbedded. Data will be presented to demonstrate the effect of the crystallite size on the properties of the material. The possibilities to cover a larger range of different materials for various applications will be discussed.

2. Nanocrystalline Silicon

The nc-Si can be prepared by various plasma deposition techniques such as sputtering in an Ar/H₂ mixture, CVD from silane diluted with hydrogen to about 1 mol%, deposition of amorphous Si (a-Si) from silane and its controllable recrystallization and by chemical transport. The best control of the crystallite size and of the thickness of the grain boundaries provides the plasma chemical transport in hydrogen plasma which has been developed already thirty years ago [22]. The disadvantage of this technique is the high purity of the plasma which is required in order to obtain reproducible and high deposition rates [23]. The variables for the control of the crystallite size, the mechanical stress and, consequently of the thickness of the grain boundaries in a direct current glow discharge is the deposition temperature and the substrate bias (see Fig.1, [11]).

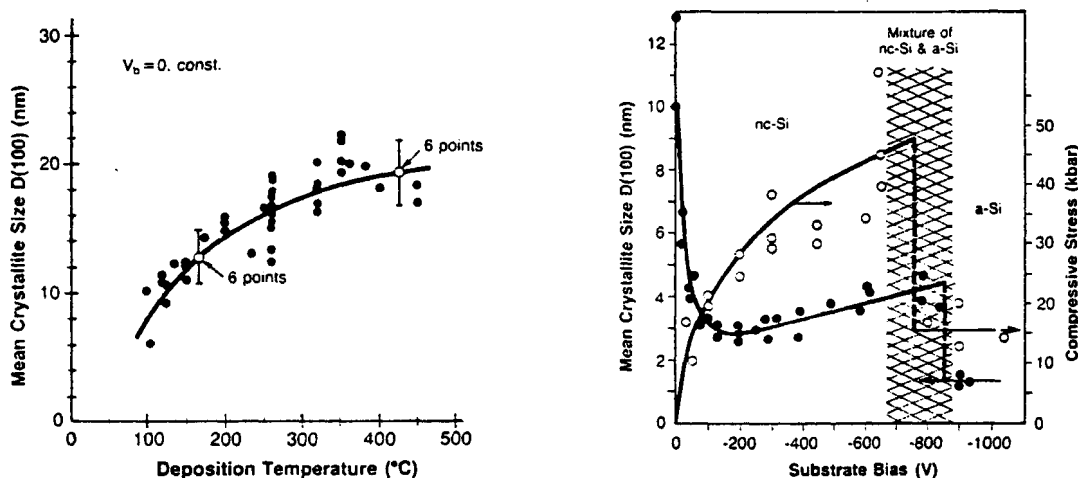


Fig. 1: Dependence of the crystallite size on **a**: the substrate temperature at floating potential and **b**: on the substrate bias at substrate temperature of 260 $^{\circ}\text{C}$ [11].

Films deposited at floating potential have a small tensile stress [10,11] which allows an easy oxidation than those deposited under negative bias [24] which show oxidation of the grain boundaries only at high temperatures. Thus, if films with thick grain boundaries, i.e. a large separation of the nanocrystals are required, deposition at low temperature and floating potential is chosen (Fig.1a) whereas appropriate combination of a negative bias and substrate temperature allows us to prepare films with the same crystallite size but only few Ångströms thin SiO_2 tissue [12,13]. The importance of the control of these parameters is illustrated by Fig. 2 [8,13].

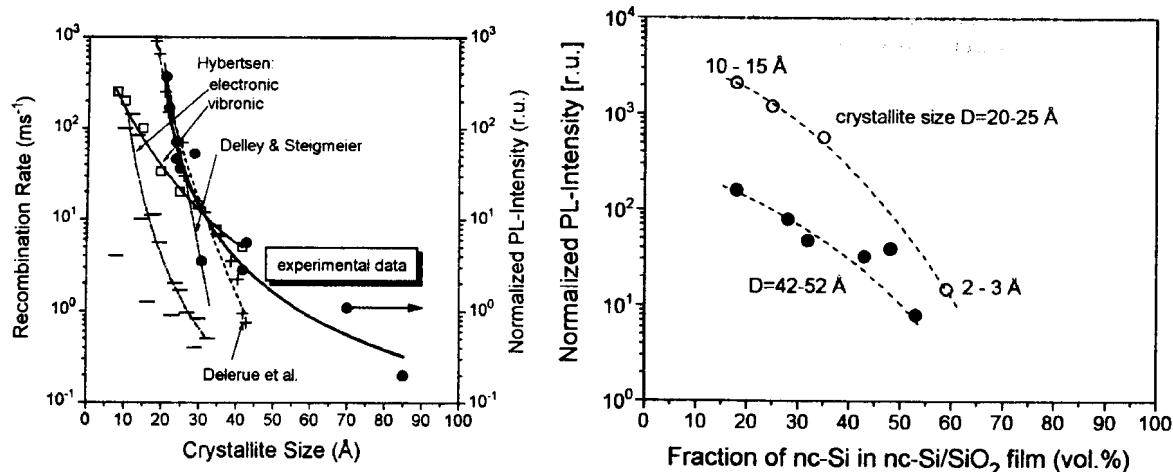


Fig.2: Dependence of the efficiency of the photoluminescence (PL) on a: the crystallite size (large separation of the crystallites) and b: on the thickness of the SiO_2 tissue [8,13].

The strong increase by about three orders of magnitude observed for crystallite sizes decreasing from about 6 to 2 nm (Fig.2a) is due to a progressive mixing of electronic states from different k -values in the Brillouin zone, and it is in a good agreement with the theoretical predictions. The reason for the strong decrease of the PL efficiency for films with the same crystallite size but decreasing thickness of the SiO_2 grain boundaries is less clear. It may be either due to the increasing probability of the tunneling of photogenerated carriers and, consequently, their decreasing localization, or to the increasing probability of non-radiative recombinations on defects in that tissue. As the discussion of these questions is beyond the scope of this paper we refer to the original literature for further details (see [13] and references therein).

3. Novel Superhard Nanocrystalline/Amorphous Composites

The theoretical concept of M. Cohen for the selection of new superhard materials is based on the idea that the bulk modulus scales with the strength and ionicity of the interatomic bond [25,26]. Based on his calculations the hardness of $\beta\text{-C}_3\text{N}_4$ should be comparable to that of diamond, and cubic BN should be softer than as expected so far from earlier simple estimates. However, the preparation of C_3N_4 requires extreme conditions (high temperature of $\geq 800^\circ\text{C}$, high density nitrogen plasma and ion bombardment) and the highest value of hardness reported so far for uniform, dense and stoichiometric C_3N_4 films reaches only 2500 kg/mm^2 [27]. Moreover, carbon and boron containing materials which deposition needs temperatures in excess of $500\text{--}600^\circ\text{C}$ are not compatible with steel substrates because of the high solubility of these elements in iron. This essentially applies to all the materials, such as polycrystalline diamond, c-BN, $\text{B}_x\text{C}_y\text{N}_z$, B_{22}O and others which are prepared primarily by plasma CVD and sputtering.

It is well known that the experimental values of the strength of engineering materials and single crystals are two to four orders of magnitude smaller than the theoretical values for the slip of crystallographic planes (which is related to the interatomic bond strength) [14,15]. In ductile materials this is due to the formation, multiplication, propagation and pile-up of dislocations which lead to crack formation and failure. In glasses and ceramics the strength is limited by the crack formation and propagation. Therefore, our concept for the design of superhard nanocrystalline/amorphous composite materials [19,20] is based on the idea how to avoid these usual mechanisms which limit the practical strength: A dislocation source cannot operate in a 2 to 4 nm small nanocrystal and any structural defect including a dislocation will, during the synthesis of the material, annihilate in the grain boundary. Should a dislocation be formed under a very high mechanical stress, it cannot move through the amorphous skeleton surrounding the nanocrystal. Only the high image stress induced by the dislocation within the amorphous phase might cause formation of nanocracks, but the propagation of the nanocracks will be hindered by the three dimensional nature of the amorphous skeleton.

Obviously, we need a less than 1 nm thin amorphous grain boundaries and a strong segregation between the amorphous and crystalline phase which will provide sharp interfaces. A moderate deposition temperature should provide a sufficient mobility of the monomers at the surface during the growth to allow the segregation on one hand but avoid mixing due to the entropy term at high temperature on the other hand. A simple thermodynamic estimate shows that in the ternary systems nc-Me_xN/a-Si₃N₄ (Me stays for a transition metal which forms thermodynamically stable nitrides, such as Ti, Zr, Hf, V, Nb, Ta and others) with a sufficient chemical activity of nitrogen the segregation will occur at temperatures below 800°C. At a temperature of 400-500°C, which is compatible with steel substrates, the transition metals form crystallite deposits whereas Si₃N₄ remains amorphous due to its complex crystal structure. Plasma CVD is the technique which will provide all these requirements. Our concept should work with many combinations of a strong nanocrystalline material and amorphous skeleton (e.g. a-AlN instead of Si₃N₄).

The plasma CVD of nc-TiN/a-Si₃N₄ has been done from titanium tetrachloride and silane diluted with hydrogen and nitrogen [19,20] at a substrate temperature of about 500°C. The hardness indeed increases with decreasing size of the TiN nanocrystals. The highest value of about 5 000 kg/mm² is obtained at a silicon content of about 8 at.%, i.e. in the range of the percolation threshold for Si₃N₄.

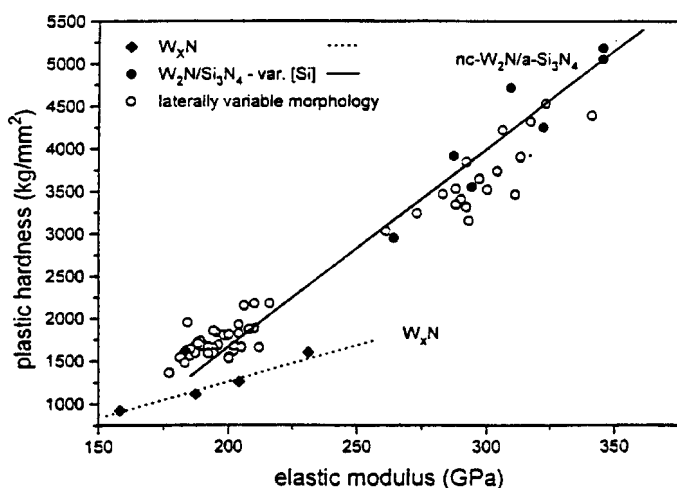


Fig.3: Correlation between the hardness and elastic modulus of nc-W₂N/a-Si₃N₄ with a various content of silicon nitride.

In order to verify the general validity of our concept we continue our investigation into other systems. It was challenging to try a transition metal nitride which free energy of formation is significantly less than that of the nitrides mentioned above. The obvious candidate was tungsten which forms W_2N and WN. The latter decomposes at 550°C even under a high nitrogen pressure and the partial pressure of W_2N exceeds 0.1 mbar at 300°C. In spite of these unfavorable properties the hardness of that material reaches 5 200 kg/mm² (see Fig.3) and higher values are probably possible. Interesting is the large fraction of elastic recovery after the indentation experiment which reaches a value of almost 80%. For comparison, the much softer "hard a-C:H" („diamond like carbon", about 2 000 kg/mm) shows elastic recovery of 70-90 %.

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