FORMATION MECHANISM OF AMORPHOUS Ni-P THIN FILMS

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Growth stages of amorphous Ni-P films deposited both by electrolytic and by chemical means were studied by electron microscopy. Nucleation and the growth of separated three dimensional grains have been proved.

Comparing the shape of grains with that of computed ones different mobilities of adatoms on the surface of growing grains have been found. The mobility of adatoms is promoted in the case of electrolytic deposition. The development of structural inhomogeneities ("supernetwork") can be attributed to the coalescence of grains as well as to the limited mobility of adatoms, building the amorphous structure of the grains.

Introduction

Extensive studies of amorphous films — especially of semiconductor and metallic ones — have unambiguously shown that a general characteristic of these films is a certain kind of structural inhomogeneity [1—9]. This structural inhomogeneity constitutes a quasi-periodical network, and can be visualized by means of phase contrast electronmicroscopy or by low-angle electron diffraction.

Some authors considered this network as a system of cracks [6, 7]; others [8, 9] basing their views in the first place on the investigation of amorphous Ge, amorphous Si and CoGd layers, regarded it as a region of lower density of the continuous amorphous network, a "supernetwork" [8, 9] where most of the atomic voids had accumulated. The correctness of the latter assumption was confirmed by the result of an in situ heat treatment of high purity amorphous Ge layers [3]. Thus this particular inhomogeneity in amorphous Ge layers can be heat treated. In the course of real structural rearrangement migration of the atomic voids takes place accumulating in bubbles that can be demonstrated unambiguously by means of electron microscopy. The bubbles thus formed are

created principally in the original supernetwork. The rearrangement of the amorphous structure can be considered as indirect proof confirming that the supernetwork represents the region of accumulation of the atomic voids. A further justifiable assumption is — though to our knowledge no results of measurements to prove this directly have yet been published — that in the case of films having several components beside a change in density also the change in composition can be assigned to the supernetwork [9, 10].

Today it is well-known too, that the presence of structural heterogeneity and its characteristics strongly influence both the physical and chemical properties of the amorphous films (electrical conductivity in a-Ge films [11], hardness and corrosion properties of amorphous Ni-P deposited from aqueous solution [12]).

It is understandable therefore that recently increasing attention has been given not only to the determination of the real structure of amorphous films but also to the description of the formation of structural inhomogeneities. The earliest concept concerning amorphous Ge films originates from GALEENER [2], and one of the present authors developed further this model of formation of amorphous films [8]. According to this conception the formation starts with nucleation, and continues with the growth and then with the coalescence of the grains [13]. The area of the supernetwork is constituted by the regions of coalescence of grains. Thus this model takes into account the mobility of the atoms arriving at the substrate and condensing there in that case too when amorphous nuclei are formed. GUTZOV [14] and NEUMAN [15] found by thermodynamical considerations that when nuclei contain few atoms the formation of amorphous structure is more advantageous energetically. The same result was earlier obtained by GRIGOROVICI and coworkers [16] for amorphous Ge when the free energy had been calculated for different possible bond types. BARNA et al [13] simulated with a computer the change in the shape of grains growing from the solid amorphous nuclei condensed from the vapour phase. Their results represent well the effect of different supposed mobilities of adatoms on the surface of the substrate or on that of the forming amorphous grain, respectively, on the growth, the compactness and the change in shape of grains. Their results also reflect well the properties of different materials. In the case of amorphous Ge the adatoms practically cannot migrate along the periphery of the amorphous grain, thus two-dimensional grains of arm-like structure will be developed. In the case of Se and Sb films the individual adatoms should have relatively high mobility on the surface of the amorphous grains, because three dimensional cup shaped grains will grow.

Authors constructing other models for the formation of the inhomogeneous structure reflecting essentially a columnar structure, suppose that the condensing atoms are not mobile neither on the surface of the substrate nor on the surface of their developing amorphous grains [17, 18].

By computer simulation of the process they have shown that the shadow effect alone can be responsible for the columnar structure if the atoms are represented by hard spheres.

STAUDINGER and coworkers [7] have suggested on the basis of electrolytically prepared amorphous Ni-P films that the supernetwork is a crack network, and they assumed that it is developed according to the model of GALEENER [2]. BARNA et al [19] showed that during the initial period of layer formation three-dimensional grains grow up in these films deposited electrolytically and chemically.

The present authors have examined in detail the formation mechanism of the amorphous Ni-P films deposited by electrolytic and chemical means. This paper summarizes the results of the investigations.

Experimental methods

The films were prepared, in the case of chemical deposition, either on clean glass slides or on slides coated with collodium and C film, as well as on microgrids. In the case of electrolytic deposition they were deposited on an OFHC copper strip or on 100 nm thick Al film previously prepared by vacuum evaporation on microscope slides. The surface of the copper strip has been treated before preparation of the layer by chemical etching; the surface of the Al layer had been treated in $NaOH$ and H_2SO_4 and rinsed in distilled water. In the case of chemical deposition the surface of the substrates was activated by the method known from the literature [20]. Chemical deposition took place at 90 °C. The electrolytic deposition was made from a solution containing $NiCl_2 + NiSO_4$ at 75 °C, at current densities of 5 and 50 mA/cm^2.

For the purpose of TEM investigations the films were first coated with a thin layer of C (of thickness of about 10 nm), then separated from the substrate. This took place by dissolution of the colloidium or of the Al layer (the latter in 20% $NaOH$ solution at 80 °C). From the copper foil the layer was separated in $NH_4OH + H_2O_2$.

Experimental results

Chemical deposition

Fig. 1 shows the different stages of film formation. In Fig. 1a the discrete nuclei and isolated grains grown from them can easily be seen. Nucleation of the Ni-P layer is uneven, inhomogeneous. The individual grains, proved to be amorphous by electron diffration, show a certain amount of polygonization. Their growth is not the same in the different directions. In general, growth is
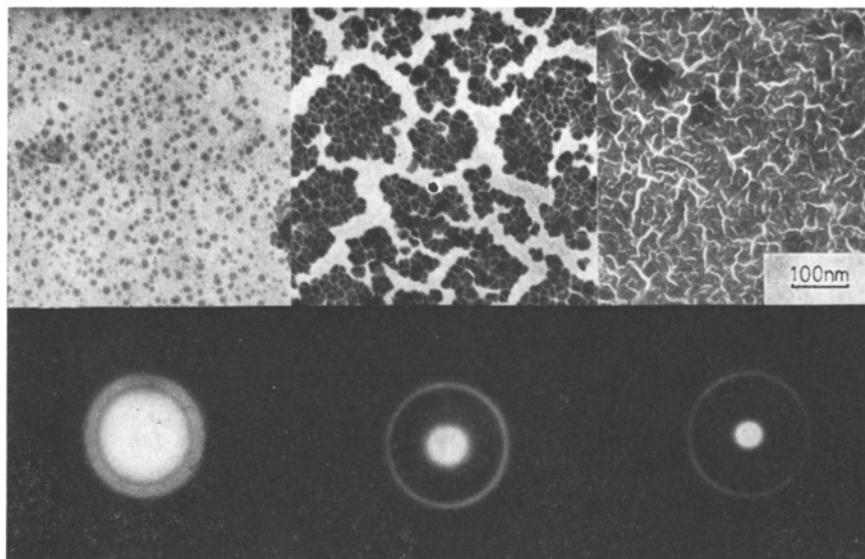
Fig. 1. Stages of the formation of a-NiP films prepared by chemical deposition

limited in the direction of the neighbouring grains, indicating thereby that the collection zone had been reduced by the neighbouring grain.

Fig. 1b shows the state of grain coalescence. It seems as if only a few contacting grains grew together by the way that their amorphous networks became connected to each other, i. e. the amorphous structure was able to become continuous. Most of the grain boundaries had sharp outlines indicating the presence of real gaps or cracks.

In the continuous films essentially three kinds of inhomogeneities are present (Fig. 1c): the coalescence zones that may be considered as reduced in density and/or in thickness; the coalescence cavities or holes formed along them [21]; the real cracks.

Electrolytic deposition

Structures characteristic of the individual stages of film growth can be seen in Fig. 2. Formation starts here also with nucleation and the growth of discrete grains (Fig. 2a). The grains present a nearly regular cup-shape form. On contact the amorphous networks developed in the grains grow together, then become continuous. However, contrast indicating the decrease of thickness or density may be observed in most coalescence zones.

In Fig. 2a where also the coalescence of some grains started, the formation of coalescence zones and cavities can be observed as well. This is similar to the process found in Sb layers [22].
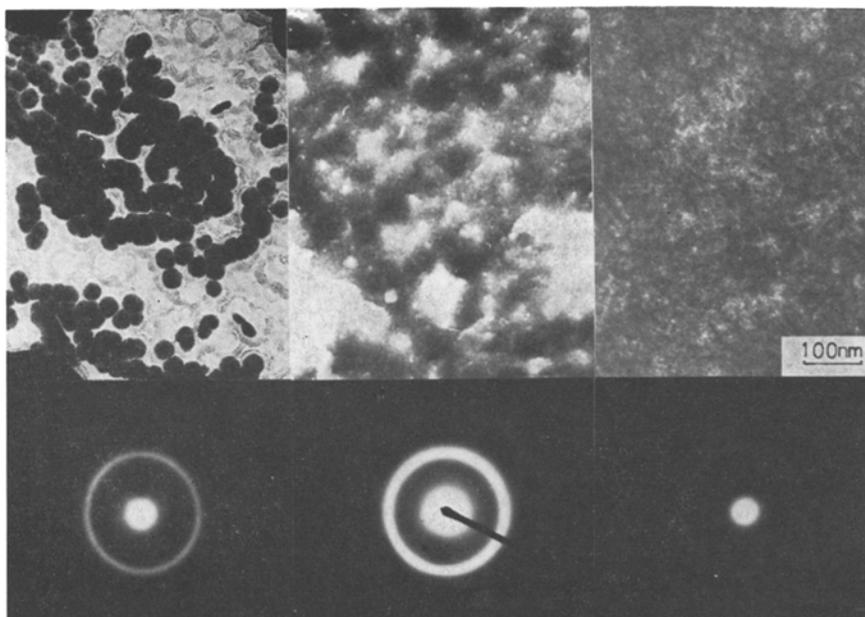
Fig. 2. Stages of the formation of a-NiP films prepared by electrolytic deposition

The already continuous layers are decorated by coalescence cavities, however, the contrast of the supernetwork representing the coalescence zones of the grains can be well distinguished, too (Fig. 2c). The cracks giving a definite, sharp outline, being so characteristic of the films formed by chemical deposition, are entirely missing here.

Conclusions

— The initial stage of formation of amorphous Ni-P films may be described in terms of nucleation, growth of three-dimensional discrete grains, then in terms of their coalescence in the case of both electrolytical and chemical deposition [23]. These results confirm the assumptions of MARTON et al [23] and STAUDINGER et al [7].

— Structure and morphology of the formed layers are determined by these processes. The inhomogeneities exhibiting the network system of lower density or thickness, the cracks and/or cavities develop during the coalescence of the amorphous grains.

— Analysis of the shape of the grains indicates that the mobility of the adatoms on the surface of the amorphous grains differs with the two methods of preparation. BARNA et al [13] have demonstrated in their computer simulation of the growth of the amorphous grains that the condition for developing
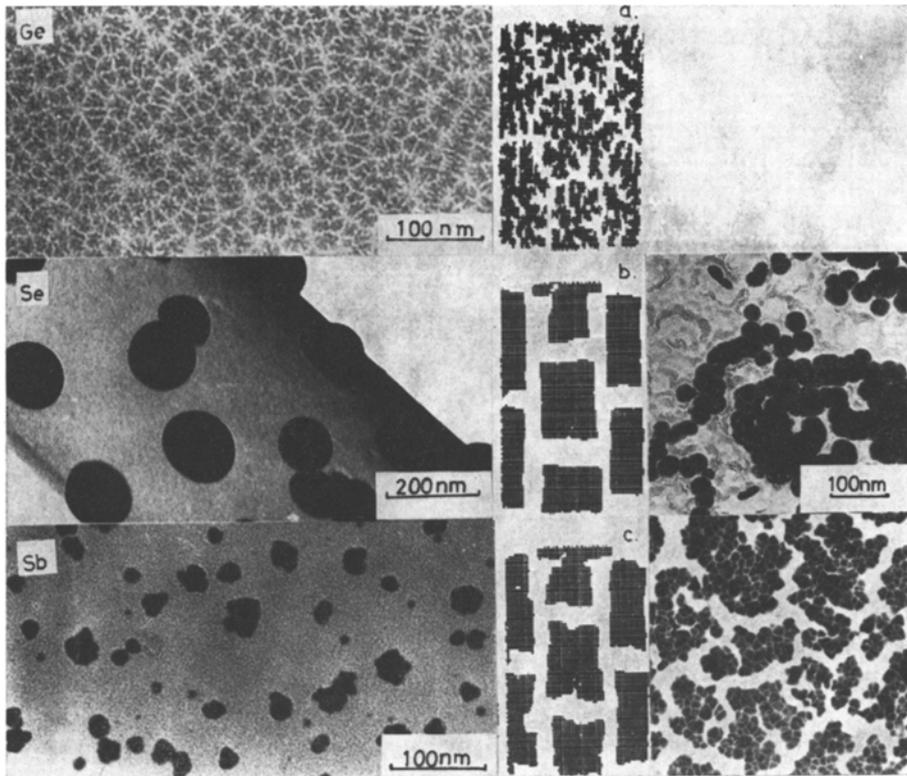
Fig. 3. The effect of adatom mobility on the shape of growing grains: Column I: grains of a-Ge (a), pure Se (b) and contaminated Sb (c) films, respectively; Column II: grains developed by computer simulation [13] by changing the mobility of adatoms; Column III: grains of a-NiP films developed by electrolytic (b); and by chemical (c) deposition

grains of regular cup-shape is the relatively high mobility of the adatoms. Thus in the case of electrolytic layer deposition one has to assume a relatively high mobility of the adatoms, whereas in the case of chemical deposition the mobility of the adatoms must be very limited. Fig. 3 shows the stage of the nucleation process of amorphous Ge, Se and Sb films in comparison with the chemical and electrolytic deposited Ni-P films and with the computer simulated ones [13] with low, high and medium adatom mobilities, respectively.

— The grains developed in the case of chemical deposition are three-dimensional although a very low mobility of the adatoms had been supposed. Based on the computer simulation [13] in that case the two-dimensional growth of indented grains should have been observed. The fact that it is not so can be explained by assuming that here "condensation" (deposition) of the adatoms constituting the film occurs only at preferred activated places, and not on the entire substrate surface. The nucleation begins at these active centres of the substrate surface and later on the places of further deposition will already be
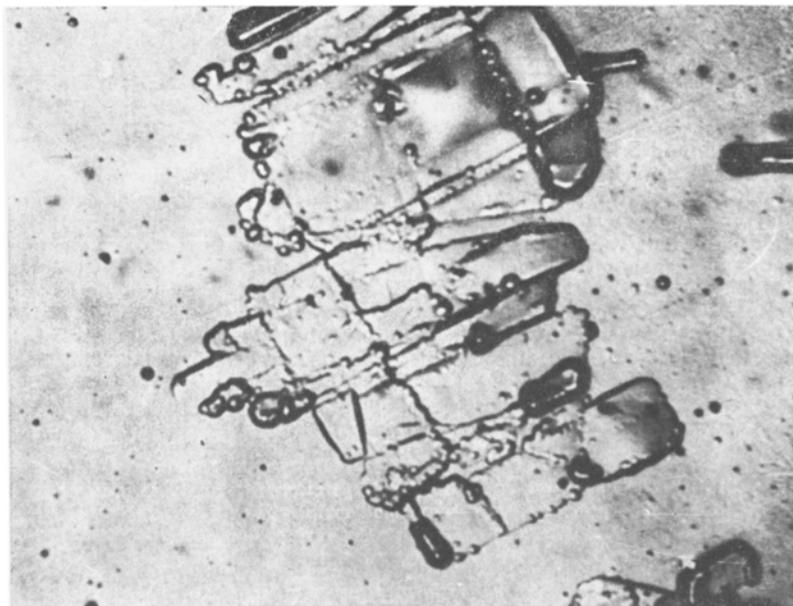
Fig. 4. Preferential nucleation of amorphous NiP on the surface of a crystalline inclusion in an amorphous CoP film

the Ni-P grains themselves. Fig. 4 shows nucleation starting on the surface of a crystalline inclusion formed in an amorphous CoP film. It can be clearly seen that the nucleation of amorphous phase begins at some preferred places of the crystal.

— The surface mobility of the adatoms controls the mechanism of grain coalescence also when preparing amorphous Ni-P films. The structure of the coalescence zone will be significantly different from the structure of grains in the case of limited mobility of the adatoms (chemical deposition), similarly, for example, to the amorphous Ge films [3]; a smaller structural difference will be created in the case of higher mobility of the adatoms (electrolytic deposition), similarly to the Sb or Se layers [22].

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