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BEHAVIOUR OF GOLD METAL AS AN IMPURITY FOR THE CHEMICAL VAPOUR DEPOSITION OF TITANIUM NITRIDE WHISKERS ON QUARTZ GLASS

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The role of gold metal for whisker growth of TiN according to reaction

$$TiCl_4 + 1/2\ N_2 + 2\ H_2 \longrightarrow TiN + 4\ HCl$$

was investigated, and it was concluded that the gold metal reacted at growth conditions with quartz glass to give an Au-Ti-Si alloy which was an important liquid phase in VLS growth of TiN crystals.

It is well known that the presence of an impurity metal has an excellent effect on whisker growth in chemical vapour deposition (CVD), and frequently its role can be explained in terms of formation of a liquid phase from which whiskers grow through a VLS mechanism[1].

The present authors have found that whisker growth of interstitial compounds of titanium and zirconium on a quartz glass could be effected in particular in the presence of gold metal. The optimum temperature for the reactions was, in general, about 1000°C. However, no evidence for the presence of a liquid phase at the reaction temperature could be found from the published relevant two-component diagrams of Au-N, Au-C, Au-B, Au-M, M-N, M-C, and M-B[2] (where M is titanium or zirconium). If the VLS mechanism should be accepted in these cases as well, the existence of a liquid phase and its composition should be confirmed.

In this paper, therefore, the behaviour of gold metal attached on a quartz glass substrate was investigated before and during the whisker growth of titanium nitride from a gas mixture of titanium tetrachloride, nitrogen, and hydrogen (2, 9, and 89 vol.%, respectively). This reaction system was selected by reasons of easier saturation of titanium tetrachloride and the absence of competing deposition of elements such as carbon and boron in the cases of carbides and borides.

An initial transformation of solid gold, which was attached by fusion of a gold chip on the quartz glass, was observed through an optical microscope, and was shown in Fig. 1. When it was

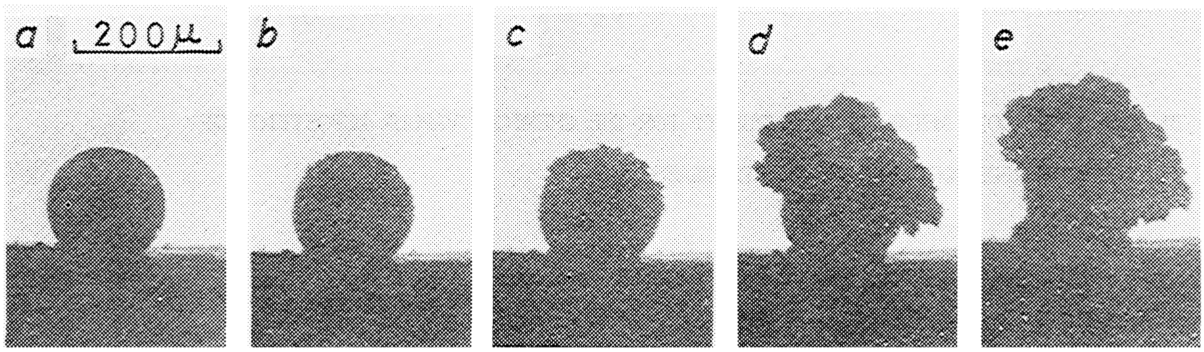

Fig. 1. Shape variation of gold metal at 1055°C. The reaction times are 0 (a), 25 (b), 27 (c), 30 (d), and 215 min. (e).

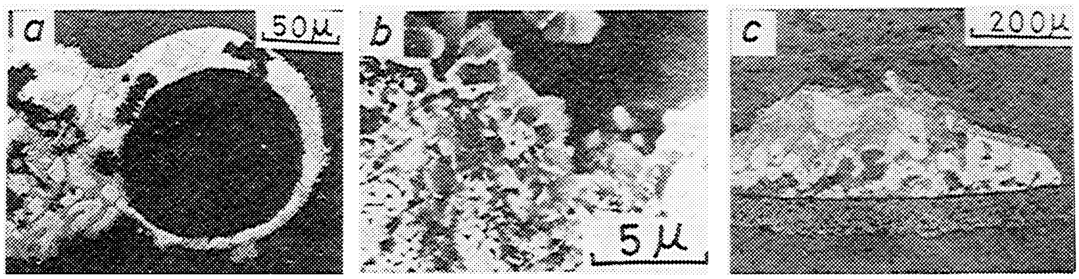

Fig. 2. Appearance of the cross sections of gold specimens held in reaction atmosphere at different temperatures: 1060 (a and b) and 1075°C (c)

exposed under a steady flow of a mixture of hydrogen and nitrogen, no change was found out (Fig. 1a). However, fine extrusions began to appear from the surface at 25 min. after the introduction of titanium tetrachloride (Fig. 1b), followed by a sudden explosive release of its bulk at 27 to 30 min. (Fig. 1c and d). The temperature range where such a phenomenon could be seen was quite narrow (1050-1065°C), which is below but near the melting point of gold metal, and at which well-formed whiskers of titanium nitride could grow by the CVD.

The appearance of the cross sections of gold specimens held at different temperatures in the presence of reagent gases is shown in Fig. 2. Below 1050°C, the specimens had little variation in the shape except a slight extrusion of its inner part. At 1060°C the whole interior material flushed out remaining a spherical shell (Fig. 2a) which might be made from TiN crystallites wetted by a liquid like layer (Fig. 2b), and above 1070°C, where TiN whiskers could not be obtained, the specimen was fused to wet the surface of substrate (Fig. 2c).

These observations strongly suggest that even below the melting point of gold metal there does exist a liquid-like phase. However, any component of the reaction species can not lower the melting point of gold as mentioned earlier. Even if titanium metal was dissolved into gold, the melting point might be raised, since Au-Ti system is peritectic but not eutectic. Therefore, the presence of another elements should be taken into account to explain the formation of a liquid phase including gold metal at growth conditions.

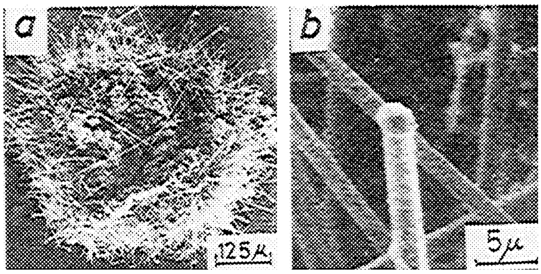

Fig. 3. (a) Whiskers grwon on a gold droplet at 1065°C for 8 hrs.:(b) a cap on the whisker tip

Fig. 3a shows a typical appearance of TiN whiskers grown on a gold droplet by reaction for 8 hrs. at 1065°C. They had sometimes liquid-like caps on their tips (Fig. 3b), suggesting that the tip-VLS growth could be operative, although foot-VLS mechanism might be applied for the growth of other whiskers which had no caps. A part of the cross section of the foot part layer is shown in Fig. 4a, where an efflux of gold alloy can be seen. Its central part (blocked in Fig. 4a) is enlarged in Fig. 4b, of which X-ray microanalysis was carried out about Ti-Kα (Fig. 4c), N-Kα (4d), Au-Mα (4e), and Si-Kα (4f). These results demonstrate the distribution of TiN and gold alloy as shown in Fig. 5. The presence of an unexpected Au-Si phase is of great interest in respect that it has an extraordinary low eutectic point (370°C) where the silicon-content is 4.5 wt.%[3]. Although a system Au-Ti is peritectic,

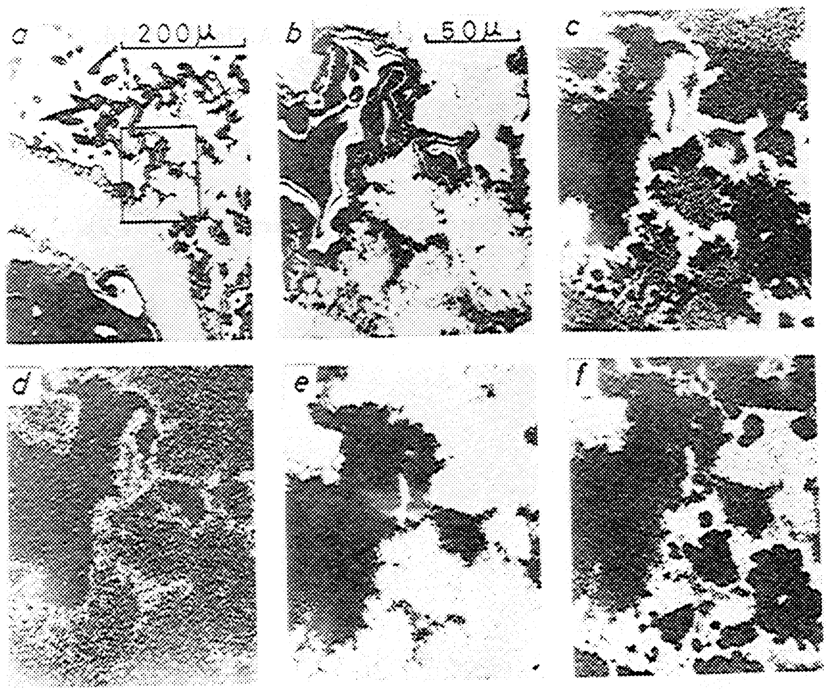

Fig. 4. Scanning electron microphotographs (a and b) and X-ray microanalysis of the cross section of the droplet: Ti-Kα (c), N-Kα (d), Au-Mα (e), and Si-Kα (f)

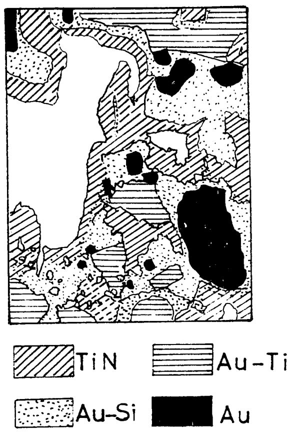

Fig. 5. Phase distribution derived from Fig. 4

the liquid phase may be extended to the lower temperature than the melting point of gold by the additional introduction of silicon to its own phase*. The distribution shown in Fig. 5. corresponds to that at room temperature, but not at growth condition, since the analysis was performed after cooling. Therefore, the phases which are present at growth conditions may consist of TiN solid and Au-Ti-Si liquid. During the gradual cooling, Au-Ti alloy, Au metal, and Au-Si eutectic mixture may segregate in turns from the **Au-Ti-Si l**iquid phase. The presence of an induction period before the explosive efflux from solid gold would be related closely to the reaction time between Au-Ti alloy and quartz glass. It may be concluded that silicon atom was an indispensable component, in the presence of which gold can play the role of a liquid phase in VLS growth of TiN whiskers. In the growth of other interstitial compounds also, a similar quartz glass effect can be expected.

* DTA analysis of the three-component system, in which titanium metal was added to the eutectic mixture of Au-Si (m.p. 370°C), showed a large heat absorption and release at 940-950°C on heating and cooling cycles, respectively, and no peaks below the temperature, indicating the presence of an Au-Ti-Si alloy melting at about 940°C.

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3) M.Hansen, ibid., second supplement (1969), p. 232.

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