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Comment on "Chemical nature of phosphorus in Ni-P deposits"

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The apparent contradiction between the initial chemical state of Ni-P deposits of Randin *et al.* and Pai *et al.* is explained. The presence of free phosphorus is shown to depend on the deposition temperature. The changes of dc resistivity upon heating is claimed to be due to crystallization and to the formation of Ni₃P regions in the films.

Electroless Ni-P deposits have been studied quite extensively in the past, showing differences in the initial state of fresh deposits.¹⁻⁸ The differences are believed to be caused in part by the variations in deposition conditions. For example, the initial structure can be readily effected by the deposition temperature. As a rule, one may not compare the initial chemical nature and structure of fresh deposits, without due regard to the precise deposition conditions.

In a previous publication⁹ we proposed that the initial state of our deposits is most likely to be single-phase polycrystalline nickel in which the phosphorus is substitutionally dissolved. This was criticized by Randin in preceding paper,⁹ based on an earlier work.⁷ In it Randin *et al.*⁷ used Ni-P alloy prepared at 94°C in a nickel chloride solution. In contrast, our samples were deposited on activated glass substrates at 23°C in a nickel sulphate solution.

Randin *et al.* found their material in the fresh state to be Ni + Ni₂P with less than 0.5 wt% of free P. Upon heating, two reaction areas in their DTA study were observed.⁵ One area above 300°C was suggested to be the reaction Ni₂P + Ni → Ni₃P, while the other at a lower temperature was attributed to the reaction of a small amount of phosphorous (<0.5 wt%) with the nickel, in which it is present as a solid solution, to produce a nickel phosphide Ni₂P and/or Ni₃P.

If we assume no other difference between our respective experiments, but the different deposition temperatures, also if we take the total P content in both deposits to be 7.8 wt% and if we take the activation energy¹⁰ for the reaction 2Ni + P → Ni₂P to be 15 kcal/mole, then a quick calculation shows that the free P in our deposit should be over 99% of the total phosphorus content. In the calculation we use the expression $N_1/N_2 = \exp(-E/kT_1 + E/kT_2)$, where N_1 and N_2 are the Ni₂P populations at temperatures T_1 and T_2 , respectively. In the expression, E is the activation energy for the formation of Ni₂P from Ni and P and k is Boltmann's constant. A substitution of E , k , and $T_1 = 296^\circ\text{K}$, $T_2 = 367^\circ\text{K}$ yields $N_1/N_2 = 0.0072$. Randin's figure for the free P in their deposits ($T_2 = 367^\circ\text{K}$) of <0.5 wt%, gives $94\% < N_2 < 100\%$ of the total P content. With this, we get the Ni₂P population $N_1 = 0.0072N_2$ in our deposits ($T_1 = 296^\circ\text{K}$) to be $0.68\% < N_1$

<0.72% of the total P content. Thus over 99% of the total P content remains free in our fresh deposits. This is clearly in agreement with our previous suggestion. It should be noted that the present calculation is made on the basis of Randin's results.

On heating these Ni-P films we measured the dc resistivity and analyzed the observed changes in terms of grain-boundary annealing (growth of the crystallites) and the formation of Ni₃P regions. The former leads to a decrease in resistivity while the latter increases the resistivity via two separate mechanisms. First, the formation of Ni₃P takes three nickel atoms away from metallic conduction and second, the growth of high-resistivity (120-μΩ cm room-temperature resistivity¹¹) Ni₃P crystalline regions causes film inhomogeneities. The inhomogeneous regions restrict the flow of current to channels, thus the resistivity increases. For very thin films this effect is more pronounced than for thick ones, in agreement with our experiments (see Fig. 7 in Ref. 8).

The two processes considered in our original work are thermally activated ones. The activation energies have been found to depend on temperature and film thickness. Also the coefficients in the two resistivity terms [see Eq. (5) in Ref. 8] are film-thickness dependent. The temperature and film-thickness dependences of the above quantities take care of any intermediate process that may occur during heating, such as the formation of Ni₂P. However, as we had no direct evidence of intermediate states, we did not consider them in our analysis.

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