

Substrate(Ni)-Catalyzed Electroless Gold Deposition
from a Non-Cyanide Bath Containing
Thiosulfate and Sulfite

M.Kato^a, J.Sato^b, H.Otani^b, T.Homma^b,
Y.Okinaka^c, T.Osaka^{b,c,d}, and O.Yoshioka^e

^aKanto Chemical Co., Soka-shi, Saitama-ken, Japan,
^bDepartment of Applied Chemistry, ^cAdvanced Research
Center for Science and Engineering, ^dKagami Memorial
Laboratory for Materials Science and Technology,
Waseda University, Shinjuku-ku, Tokyo, Japan,
^eHitachi Cable Co., Hitachi-shi, Ibaraki-ken, Japan

Substrate-catalyzed electroless gold plating, as distinguished from the conventional galvanic displacement and autocatalytic processes, was first described by Iacovangelo and Zarnoch¹. Their bath contained $\text{KAu}(\text{CN})_2$ as the source of gold and hydrazine as the reducing agent in a strongly alkaline medium consisting of KOH, KCN, and K_2CO_3 . In this system electrons needed to reduce $\text{Au}(\text{CN})_2^-$ ions to gold metal are provided by the anodic oxidation of hydrazine, which takes place only on the nickel substrate and not on gold. We previously performed an extensive evaluation of this system², and noted the following distinct advantages: (1) the bath is highly stable compared to autocatalytic processes, and (2) the porosity of the gold film produced is significantly lower than that of the gold film plated by galvanic displacement. The disadvantage is that the bath contains free cyanide ions and is highly alkaline, the conditions which are incompatible with conventional positive photoresists employed to delineate circuit patterns.

To overcome the disadvantage of the cyanide bath, we attempted to develop a non-cyanide, substrate-catalyzed bath containing thiosulfate and sulfite by modifying the autocatalytic baths containing the same ligands^{3,4}. During the initial search for a reducing agent which is catalytically oxidized only on Ni and not on Au, it was observed, using electroless NiB as the substrate, that gold deposition takes place from a thiosulfate-sulfite bath even without adding any reducing agent. (For the composition and operating conditions of the basic bath used in this study, see Table 1.) This phenomenon was previously discovered by Krulik, Mandich, and Singh^{5,6}, who claimed that the reaction of gold deposition from this system is autocatalytic. We made a detailed mechanistic investigation of this system, and found that the gold deposition reaction actually consists of both substrate-catalyzed and galvanic displacement reactions. We also conducted a series of experiments to optimize bath composition, substrate composition, and pretreatment conditions to obtain practically useful gold films which are uniform and adherent. This paper reports results of these investigations.

Reaction Mechanism – That the gold deposition reaction observed on Ni substrate was not autocatalytic was apparent from the fact that no gold deposition took place on a piece of gold sheet immersed in the bath. To find whether galvanic displacement is involved in the gold deposition on Ni, the amount of nickel dissolved in the bath was determined, and the amount of gold equivalent to the dissolved amount of nickel was calculated and compared with the actual amount of gold deposited. It was found that the quantity of dissolved nickel accounts

for approximately 20% of the total amount of gold deposited under the specific set of conditions used, the remainder being attributed to the substrate-catalyzed reaction. The extent of contribution of each of the two types of reactions actually depends on the concentration ratio of thiosulfate to sulfite in the bath. The concentration ratio was also found to affect the rate of gold deposition, appearance of the gold deposit, and the maximum gold thickness that can be deposited.

To find which species serves as the reducing agent in this system, electrochemical polarization measurements were carried out on a NiB electrode immersed in various solutions. The results unequivocally showed that sulfite ions function as the reducing agent in the substrate-catalyzed gold deposition reaction.

Effect of substrate composition – The uniformity and adherence of deposited gold were found to depend on the composition of Ni substrate. On electroless NiB films it was necessary to decrease the concentration of thiosulfate from 0.08M for the basic bath to as low as 0.01M to produce uniform deposits. On electroless NiP films, uniform and adherent deposits were obtained from the basic bath only when the P content was low (4.7 wt%). On high P content (15.4 wt%) NiP films we failed to produce satisfactory gold films in spite of the introduction of various pretreatment processes.

Porosity of gold deposits – Gold films deposited from the substrate-catalyzed bath were found to be much less porous than those produced by galvanic displacement. Very significantly, the porosity of the gold deposits from the present system was found to decrease by *decreasing* the thickness from 0.28 μm to 0.05 μm , provided that a sufficient time is allowed for the thickness to reach the maximum value obtainable in the given bath. An essentially pore-free gold film was obtained at the thickness as low as 0.05 μm .

References

1. C.D.Iacovangelo and K.P.Zarnoch, *J. Electrochem. Soc.*, **138**, 983 (1991).
2. T.Osaka, T.Misato, J.Sato, H.Akiya, T.Homma, M.Kato, Y.Okinaka, and O.Yoshioka, *ibid.*, **147**, 1059 (2000).
3. T.Inoue, S.Ando, H.Okudaira, J.Ushio, A.Tomizawa, H.Takehara, T.Shimazaki, H.Yamamoto, and H.Yokono, *Proc. 45th IEEE Electronic Components Technology Conf.*, 1059 (1995).
4. M.Kato, Y.Yazawa, and Y.Okinaka, *Proc. AESF Technical Conf., SUR/FIN '95*, pp. 805-813 (1995).
5. G.A.Krulik and N.V.Mandich, U.S.Patent 5,232,492 (1992).
6. G.A.Krulik, N.V.Mandich, and R.Singh, U.S.Patent 5,318,621 (1994).

Table 1
Basic bath composition and operating conditions
for substrate-catalyzed gold deposition

$\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$	0.01 M
Na_2SO_3	0.32
$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	0.08
Na_2HPO_4	0.32
pH (NaOH)	9.0
Temperature	60°C

