

Effect of Amine Borane Structure on Activity in Electroless Plating

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The effect of substituents on the activity of amine boranes in nickel electroless plating has been studied. The minimum coverages of evaporated palladium, silver, gold, and copper catalysts necessary for initiation of plating by solutions incorporating these reductants have been determined. A dissociative mechanism for nickel electroless plating with amine boranes is proposed. A relationship between the strength of the donor-acceptor (N-B) bond and minimum coverage of catalyst necessary for initiation of nickel deposition is proposed.

INTRODUCTION

Amine boranes have been widely used as reducing agents in aqueous and non-aqueous solvents, as well as polymerization catalysts, antioxidants, and stabilizing agents. For more than a decade, sodium borohydride or amine boranes have also been used as reductants in electroless plating. This process has found many applications in metallurgy and the electronics industry. One of the latest applications of electroless plating is the use of this process as an amplification step (i.e., physical development) in imaging systems (1). Nickel electroless plating baths containing amine boranes, particularly dimethylamine borane (DMAB), are finding increasing use. A properly formulated electroless plating bath is thermodynamically unstable, but kinetically stable; its decomposition leads to the deposition of metal. This process occurs only in the presence of a catalyst. Palladium is the most commonly used catalyst for initiation of electroless plating.

A detailed study of the interaction of dimethylamine borane with evaporated palladium films carried out in this laboratory indicated that DMAB undergoes catalytic decomposition with elemental

boron as a final product (2). According to the mechanism proposed for this reaction, catalytic decomposition of DMAB proceeds through the cleavage of the N-B bond. On the basis of these studies, it has been proposed that the energy of the N-B bond and the ability of a catalyst to facilitate its cleavage are the critical parameters for the initiation and propagation of nickel physical development.

In order to test this hypothesis, studies were undertaken in which a series of methyl-substituted amine boranes were employed as the reducing agents for nickel physical development. The critical (minimum) coverages of catalyst necessary for initiation of metal deposition were determined. While the amine boranes have been used fairly extensively in nickel deposition processes, little is actually known of the actual effect of the amine structure on the reactivity of the borane reductant in such solutions. Of particular interest is the minimum catalyst coverage (critical size of catalytic centers) necessary for initiation of metal deposition and the rate of the deposition processes. The minimum number of atoms or molecules of a given material (critical size) that are able to form a catalytically active center is taken as a measure of the catalyst activity.

EXPERIMENTAL SECTION

Ammonia borane (H_3NBH_3), mono-methylamine borane ($\text{CH}_3\text{H}_2\text{NBH}_3$), dimethylamine borane ($(\text{CH}_3)_2\text{HNBH}_3$), and trimethylamine borane ($(\text{CH}_3)_3\text{NBH}_3$), were supplied by Callery Chemical Co. and purified by recrystallization from butyl chloride. For all reducing agents, a nickel-pyrophosphate-ammonia electroless plating bath of the following composition has been used (3): $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 25 g/liter; $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, 50 g/liter; adjust pH to 10.5 with NH_4OH ; $\text{Me}_{3-n}\text{H}_n\text{NBH}_3$ reducing agent, 0.17 M.

The palladium, silver, gold, and copper catalysts used in this work were prepared as thin metallic films deposited on microscope slides by vacuum deposition (4). Evaporations were carried out under 1×10^{-6} Torr pressure using Al_2O_3 -coated Ta (0.10-in.) resistively heated boats as evaporation sources. Coverages of the catalysts ranged from 1.6×10^{-9} g/cm² to 8.0×10^{-7} g/cm², which correspond to 9.0×10^{12} – 7.7×10^{15} atoms/cm² or 8×10^{-3} – 6.7 monolayers. Critical coverages of the catalytic materials were determined by using stepped evaporated samples (4). The catalyst coverages varied in a geometrical progression, so each step differed from the preceding by a factor of $\frac{1}{2}$. For a given condition of vacuum deposition, type of substrate, and deposited material, the sizes of metal nuclei are related to the metal coverages.

Nickel electroless plating was carried out for 30 min at room temperature. The preliminary experiments indicated that minimum coverage of a catalyst is independent of plating time, as long as plating

solution does not decompose. The rate of nickel deposition was determined using a ground-glass slide (18.6 cm²) with palladium coverage of 1.4×10^{-6} g/cm². This substrate proved to be very useful for studies of deposition of thick coatings owing to its good adhesion characteristics. The amount of nickel deposited was determined by atomic absorption spectroscopy after the metal coatings were dissolved in aqua regia.

RESULTS AND DISCUSSION

A. *Critical Coverages of Pd, Ag, Au, and Cu Catalysts for Nickel Electroless Plating*

The critical coverages necessary for initiation of room temperature nickel deposition by the plating baths described above are listed in Table 1.

These results indicate that the critical coverage of a given catalyst increases monotonically with an increase in the number of methyl substituents in the amine borane. This suggests a direct relationship between the structure of an R_3NBH_3 adduct and its effectiveness as a reductant in nickel electroless plating.

The inductive effects caused by the methyl groups on the stability of amine borane adducts were shown distinctly by McCoy and Bauer (5), who determined the enthalpy of gas phase association ($\Delta H_{\text{assoc}}^0$) of BH_3 and various methylamines (Table 2).

These results demonstrate clearly that for the series of $(\text{CH}_3)_{3-n}\text{H}_n\text{NBH}_3$ the strength of the donor-acceptor bond decreases monotonically with n . Comparison

TABLE 1
CRITICAL CATALYST COVERAGES FOR VARIOUS Ni ELECTROLESS PLATING BATHS

Reducing agent (0.17 M)	Atoms/cm ²			
	Pd	Ag	Au	Cu
H_3NBH_3	3.7×10^{13}	2.83×10^{14}	1.64×10^{14}	3.4×10^{15}
$\text{CH}_3\text{H}_2\text{NBH}_3$	1.5×10^{14}	5.30×10^{14}	1.70×10^{14}	$>7.69 \times 10^{15}$
$(\text{CH}_3)_2\text{HNBH}_3$	5.8×10^{14}	1.89×10^{15}	3.14×10^{14}	$>7.69 \times 10^{15}$
$(\text{CH}_3)_3\text{NBH}_3$	$>1.7 \times 10^{16}$	$>4.5 \times 10^{15}$	$>2.47 \times 10^{15}$	$>7.69 \times 10^{15}$

TABLE 2
 KINETIC AND THERMODYNAMIC DATA ON AMINE BORANES

Amine borane	$\Delta H_{\text{assoc}}^{\circ}$ (δ) (kcal/mole)	$k_{\text{hydrolysis}}$ (γ) ($\text{m}^{-1} \text{sec}^{-1}$)	$\Delta H_{\text{hydrolysis}}$ (θ) (kcal/mole)
H_3NBH_3	-13.7		
$\text{CH}_3\text{H}_2\text{NBH}_3$	-17.5	3.5×10^{-1}	16.1
$(\text{CH}_3)_2\text{HNBH}_3$	-18.8	9.7×10^{-3}	21.2
$(\text{CH}_3)_3\text{NBH}_3$	-31.5	1.1×10^{-4}	25.7

of these data with those obtained by Ryschkewitsch (6) and Kelly, Marchelli and Giusto (7) for the acid-catalyzed hydrolysis of methylamine boranes indicates a close relationship between enthalpy and rate of hydrolysis of amine boranes and the strength of the N-B bond (Table 2).

Murray (8) proposed that the order of reactivity of amine boranes exhibited in hydrolysis, hydroboration, and reduction reactions is determined by the strength of the boron-nitrogen bond coupled with the mechanism for each type of reaction. The equilibrium dissociation of the amine borane suggested as the first step in hydroboration is a function of the Lewis basicity of the amine moiety. The same rule applies in the case of acid-catalyzed hydrolysis, which proceeds by proton displacement at the nitrogen atom. That the order of reactivity is the same in the case of nickel electroless plating suggests that it proceeds through a similar step. Dissociation takes place on the catalytic nuclei, as well as on the deposited nickel, which is autocatalytic for the electroless deposition reaction. Therefore, it is proposed that the facilitation of dissociation of the amine borane (i.e., B-N bond cleavage) is one of the primary functions of a catalyst in the course of nickel electroless plating. As was shown by Baetzold (9), the catalytic activity of metal aggregates is determined by their electronic properties, which depend on their size. It appears very likely that a small catalytic center can facilitate dissociation of the weakly bonded H_3NBH_3 adduct, but is not able to function similarly in the case of more strongly bonded methyl-substituted derivatives. The nickel electroless plating process carried

out using any of the reducing agents employed in this work is expected to proceed through the same intermediate steps. Therefore, it appears unlikely that the formation of intermediates, such as (cat-H⁻) or (cat-H₂) or electron transfer, are the primary factors determining critical size of a catalytic center.

The electrochemical potential measurements of methylamine boranes carried out in these Laboratories indicated that there is no observable oxidation wave for any of the amine boranes when platinum, pyrolytic graphite, or gold anodes were used. This supports the hypothesis of a dissociation mechanism in the oxidation of amine boranes and emphasizes the role of the catalyst in the course of this process.

The results of these electrochemical measurements are similar to those observed for the cyanoborohydride ion and have been discussed recently by Gysling (10), who emphasized the importance of differentiating between electrochemical redox reactions and the chemical redox reactions where specific mechanisms can be operative.

The influence of the reactivity of amine borane on the rate of nickel deposition (Pd-nuclei, $[\text{Me}_{3-n}\text{H}_n\text{NBH}_3]$, 0.17 M, temp, 21°C) is shown in Fig. 1. The data indicate a similar trend of the rate of nickel deposition and the reactivity of methylamine boranes in the initial stage of the process, i.e., the lower strength of the donor-acceptor (N-B) bond leads to the higher nickel deposition rate, as well as lower critical coverage of catalyst for initiation of this process (Table 1). The instability of the nickel electroless plating bath with ammonia borane as the reducing

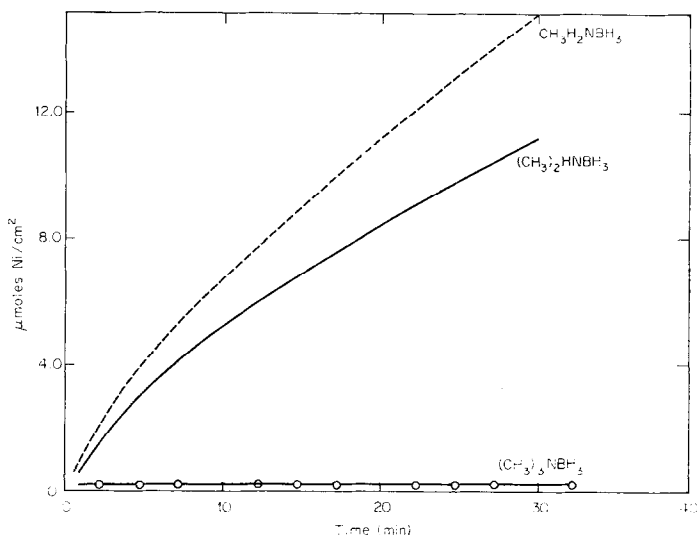


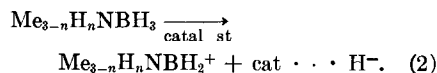
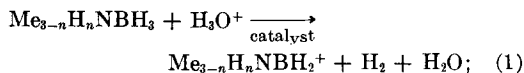
FIG. 1. Effect of amine structure on kinetics of nickel electroless plating.

agent precluded any detailed kinetic studies of this solution.

B. Characterization of Methylamine Boranes

In amine boranes $\text{Me}_{3-n}\text{H}_n\text{NBH}_3$, the character and strength of the B–N bond depends on the nature of the substituents at the nitrogen atom. The strength of the B–N bond is determined to a considerable extent by its polarity, that is, by the degree of transfer of the unshared electron pair of the nitrogen atom to the boron atom. The increase in base strength of methylamine over ammonia and the further increase of dimethylamine over methylamine are plausibly ascribed to this electronic factor. The inductive effect of the methyl groups increases the electron density on the nitrogen atom increasing the facility of electron-pair donation to a Lewis acid, such as BH_3 . Therefore, the affinity of an amine for the borane moiety increases with the introduction of the methyl groups. This phenomenon is clearly indicated by the results of MO calculations carried out by Baetzold (11) (Table 3). As a measure of base strength, one may also consider the ionization potential (as shown in Table 3) of the free base modified by polarizabilities and steric

factors arising as a consequence of a donor-acceptor compound formation. The consistency of the order of reactivity of methylamine boranes in hydroboration reduction reaction and hydrolysis, as well as the order of the strengths of donor-acceptor bonds, supports the proposal of a dissociative mechanism for these reactions. Other possible mechanisms assume that the reactions listed above, as well as nickel electroless plating, proceed through a direct attack on the B–H bond [Eqs. (1) and (2)], or through electron transfer.



This appears to be less likely when one takes into account that the order of reactivity proved to be the reverse of the order of the strengths of the B–H bond for methylamine boranes, as well as their ionization potentials, as calculated by Baetzold (11) using MO methods (Table 4). Unlike the data of Table 3, there is no correlation between reactivity and molecular constants. Note that the ionization potential of the amine boranes varies in the opposite order of the values for free

TABLE 3
MO CALCULATIONS FOR SOME AMINE BORANES

Amine borane	Electronic charge on N (e ⁻)	Ionization potential of free amine (eV)	Relative ^a N-B bond strength
H ₃ NBH ₃	-0.606	14.49	0.4728
CH ₃ H ₂ NBH ₃	-0.613	11.85	0.4798
(CH ₃) ₂ HNBH ₃	-0.716	6.20	0.4892
(CH ₃) ₃ NBH ₃	-0.876	2.47	0.5049

^a Measure of N-B orbital overlap.

amine. This observation further supports the dissociative mechanism of oxidation, as well as hydrolysis of amine boranes.

CONCLUSIONS

These studies indicate that the reactivity of amine boranes used as reductants in a nickel electroless plating follows the same order as found in hydrolysis, hydroboration, and reduction reactions. The proposed mechanisms of these reactions involve dissociation of a R₃NBH₃ adduct in one of the first steps of the reaction. Therefore, it is proposed that nickel electroless plating proceeds through a similar dissociative mechanism and that dissociation of amine boranes to the free amine and a borane radical is facilitated on the surface of a catalyst. Smaller catalytic centers are able to catalyze dissociation of a relatively weakly bonded adduct (i.e., H₃NBH₃), but larger nuclei are necessary for the same process in the case of a more

TABLE 4
MO CALCULATIONS FOR SOME AMINE BORANES

Amine borane	Relative ^a B-H strength	Ionization potential of amine borane (eV)
H ₃ NBH ₃	0.686	11.72
CH ₃ H ₂ NBH ₃	0.685	10.85
(CH ₃) ₂ HNBH ₃	0.684	3.00
(CH ₃) ₃ NBH ₃	0.683	2.79

^a Measure of B-H bond overlap.

stable adduct [i.e., (CH₃)₂HNBH₃]. Therefore, the critical size of the catalyst necessary for initiation of nickel deposition depends on the reactivity towards dissociation of the amine borane used as the reducing agent. Since this reactivity is dependent on the strength of the N-B bond, it can be modified by changing the Lewis basicity of free amine towards BH₃. The knowledge of the relationship between the structure of amine borane and the critical size of a catalytic center enables modification of the properties of nickel electroless plating baths according to the particular requirements. The proper selection of reducing agent allows one to control the properties of the electroless plating bath, such as the rate of metal deposition and stability of the bath, as well as activity of the catalyst necessary for initiation of the plating process. The variation in the critical coverage for different catalyst may be due to intrinsic differences in catalytic activity of these metals. Alternatively, these metallic films may each be characterized by a different aggregate size for constant coverage value.

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