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## Effect of Additives on the Viscosity of Liquid-Phase Dimethylaluminum Hydride

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### ABSTRACT

The effect of additives on the viscosity of liquid-phase dimethylaluminum hydride (DMAH) was investigated. The viscosity of pure liquid DMAH was measured to be 6400 centipoise (cP) and due to its high viscosity, it is difficult to vaporize DMAH effectively in a bubbler in the chemical vapor deposition of aluminum. *N,N*-Dimethyl-1-naphthylamine and *N*-ethyl-*N*-methylaniline were selected as an additive because they are a liquid at room temperature and have a high boiling point. The viscosity of DMAH was drastically reduced down to 6 cP with the addition of 3.2 mol % of *N*-ethyl-*N*-methylaniline and 8 cP with the addition of 4.3 mol % of *N,N*-dimethyl-1-naphthylamine.

Recently, metallorganic chemical vapor deposition (MOCVD) has drawn much attention as a promising process for the multilevel interconnection in ultra-large scale integration (ULSI). To date, physical vapor deposition (PVD) has been used widely for the metallization in the fabrication of integrated circuits. However, in some cases, PVD is not suitable for use in the fabrication of ULSI circuitry with a submicron feature scale due to poor step coverage. As a viable alternative over the conventional PVD metallization process, aluminum (Al) MOCVD has been studied to fill up contact or via holes in ULSI circuitry.

Dimethylaluminum hydride (DMAH)<sup>1</sup> and dimethylethylamine alane (DMEAA)<sup>2,3</sup> belong to the most promising candidates for Al MOCVD because of relatively high vapor pressures at room temperature (2.2 Torr for DMAH and 1.5 Torr for DMEAA), ability to deposit carbon contamination free films, and the advantage of being a liquid providing stable vapor pressure.

The major problem for DMAH as an Al MOCVD precursor is the lower supply rate of vapor DMAH due to the high viscosity of liquid phase DMAH, roughly estimated about 4000 cP.<sup>1</sup> Pure DMAH liquid is highly oligomerized or even polymeric, probably due to the high degree of intermolecular association of DMAH.<sup>1</sup> And also the deposition rate of Al from DMAH was reported very low with tradi-

tional bubbling technique.<sup>4</sup> Generally, the mass production in the semiconductor industry requires the supply of vapor phase precursor at high rate. Therefore, the improvement of bubbler design<sup>5</sup> or the development of performance additives<sup>4,6</sup> such as tertiary amine for effective bubbling of DMAH were proposed and investigated. We report the effect of additives on the viscosity of liquid-phase DMAH.

We selected *N,N*-dimethyl-1-naphthylamine and *N*-ethyl-*N*-methylaniline as the additives among the several tertiary amines and their molecular structure is shown in Fig. 1. These two amine compounds are liquid at room temperature and have higher or similar boiling points (*N,N*-dimethyl-1-naphthylamine: 139 °C, *N*-ethyl-*N*-methylaniline: 203 °C) compared with DMAH (154 °C). All the experiments including the addition of tertiary amine and the measurement of viscosity of liquid phase DMAH were performed under dry N<sub>2</sub> environment in a glove box at room temperature. The viscosity of liquid-phase DMAH was measured accurately from the Brookfield digital viscometer. The shelf time of liquid DMAH was about 6 months at room temperature and the purity was analyzed and confirmed from <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopy.

Figure 2 shows the effect of additives on the viscosity of liquid-phase DMAH. The viscosity of pure liquid-phase DMAH was 6400 cP. The pure DMAH is too viscous to vaporize effectively in a

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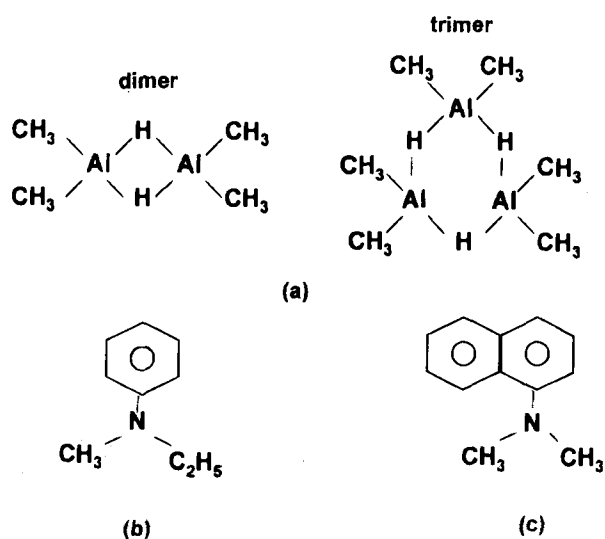


Fig. 1. Molecular structure of (a) DMAH, (b) *N*-ethyl-*N*-methylaniline, and (c) *N,N*-dimethyl-1-naphthylamine.

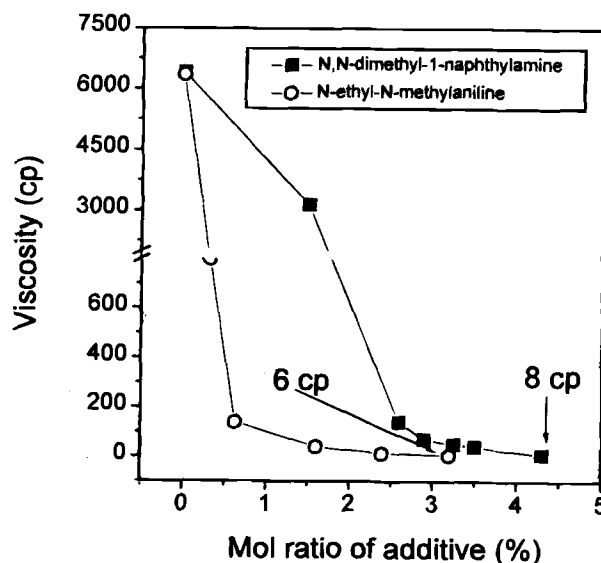


Fig. 2. Effect of the addition of *N*-ethyl-*N*-methylaniline and *N,N*-dimethyl-1-naphthylamine on the viscosity of liquid-phase DMAH at room temperature.

bubbler. And due to the high viscosity, transport of DMAH may be difficult. As shown in Fig. 2, the addition of the small amount of additive in the pure DMAH drastically reduces the viscosity of the liquid. It seems that the added tertiary amine blocks the intermolecular association of liquid DMAH. *N*-Ethyl-*N*-methylaniline is a more effective additive than *N,N*-dimethyl-1-naphthylamine. The viscosity was reduced to 6 cP with the addition of 3.2 mol % *N*-ethyl-*N*-methylaniline and 8 cP with the addition of 4.3 mol % *N,N*-dimethyl-1-naphthylamine.

We showed that the addition of a small amount of a tertiary amine such as *N*-ethyl-*N*-methylaniline and *N,N*-dimethyl-1-naphthylamine drastically reduces the viscosity of liquid DMAH. We believe that the liquid DMAH containing a small amount of additive can be used more effectively due to its lower viscosity. The effect of additive on the stability and volatility of liquid DMAH, and on the deposition rate and the deposited film quality is under investigation.

### Acknowledgment

We thank Sun-Woo Lee for assistance in the measurement and Chung Hoon Lee for assistance in the sample preparation. Financial

support from LG Semicon. and Korea Research Foundation is also acknowledged.

Manuscript submitted August 28, 1997; revised manuscript received October 23, 1997.

Pohang University of Science and Technology assisted in meeting the publication costs of this article.

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# Time-Resolved Mono-anion, Di-anion, and Solvent Transfers into a Poly(vinylferrocene)-Modified Electrode

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### ABSTRACT

We describe dynamic dual quartz crystal microbalance measurements of redox-driven ion and solvent transfers between poly(vinylferrocene) films and aqueous disodium naphthalene-1,5-disulfonate solutions. The relative transport rates are dianion > monoanion > solvent; salt does not participate. Solvent expulsion is faster than solvent entry. On short time scales during oxidation only dianion motion responds to electron transfer.

### Introduction

We describe redox switching of poly(vinylferrocene) (PVF) films exposed to aqueous disodium naphthalene-1,5-disulfonate ( $\text{Na}_2\text{NDS}$ ) solutions, and explore the competition between singly and doubly charged anions in the role of counter ions as functions of time scale and electrolyte concentration.

Polymer-modified electrode performance depends on the rate and/or extent of ion and solvent exchange between the film and the bathing electrolyte.<sup>1,2</sup> However, ion and solvent transfer (thermo)dynamics are not well understood, because purely electrochemical probes do not directly identify the species involved. Even in a 1:1 electrolyte, film switching may be accompanied by anion or cation transfer in opposite directions; the current response does not distinguish these possibilities. The electrochemical quartz crystal microbalance (EQCM)<sup>3,4</sup> has proved useful here, since film mass changes are diagnostic for anion vs cation population changes. However, in multivalent electrolytes, even the EQCM is inadequate. It responds to changes in viscosity and density that accompany electrolyte concentration changes that must be made to explore the latter's effect on film populations.

This study is novel chemically and instrumentally. First, we determine mobile species population changes for a redox polymer film exposed to an unsymmetrical electrolyte,  $\text{Na}_2\text{NDS}$ . This situation is more complex than the symmetrical electrolyte case, since it involves the transfer of more kinds of mobile species. Second, to obtain the necessary additional information, we use a dual quartz crystal microbalance<sup>5,6</sup> (DQCM), which allows exploration of the concentration variable. The present work is the first application of the DQCM to a kinetic problem. It gives absolute film mass and thus absolute ion and solvent populations within the film.

We previously studied the thermodynamics of ion/solvent partition into PVF films from 1:1<sup>7,8</sup> and 1:2<sup>9</sup> electrolytes as a function of

electrolyte concentration. In both cases, anion transfer alone satisfied electroneutrality at low electrolyte concentration (permselective conditions). Participation of cations occurred at higher concentration (nonpermselective conditions). The latter concentration regime is more complex for multivalent electrolytes, since more combinations of anion and cation transfers could satisfy electroneutrality.

Under kinetic control, PVF films in 1:1 electrolytes were transiently permselective, even when thermodynamically nonpermselective, because of differing ion transfer rates. Here we show this kinetic permselectivity phenomenon for PVF films in  $\text{Na}_2\text{NDS}$  solutions, where  $\text{NDS}^{2-}$ ,  $\text{NaNDS}^-$ , and  $\text{Na}_2\text{NDS}$  may all ultimately transfer.

### Experimental

The DQCM apparatus<sup>5</sup> and its ability to compensate for changes in liquid-phase properties<sup>6</sup> are described elsewhere. Closely matched 10 MHz AT-cut quartz crystals with evaporated Au electrodes were used. PVF films were deposited as before.<sup>10</sup> Measurements were made in aqueous 8 and 250 mmol  $\text{dm}^{-3}$   $\text{Na}_2\text{NDS}$  solutions (in which PVF films are thermodynamically permselective and nonpermselective, respectively) using methodology analogous to thermodynamic studies of this system.<sup>9</sup> For the electrolytes and conditions used, PVF films are rigid, so the Sauerbrey equation applies. Cyclic voltammetric DQCM experiments were carried out at 5 and 100  $\text{mV s}^{-1}$ . The temperature was  $23 \pm 0.3^\circ\text{C}$ .

### Results and Discussion

**Overview.**—Figure 1 shows current ( $i$ ) and mass responses ( $\Delta m$ ) to a slow ( $5 \text{ mV s}^{-1}$ ) cyclic potential sweep for a PVF film in 250  $\text{mmol dm}^{-3}$   $\text{Na}_2\text{NDS}$ . They are typical of PVF responses in aqueous media. Analogous data in 8  $\text{mmol dm}^{-3}$   $\text{Na}_2\text{NDS}$  solutions were qualitatively similar, except that the current peaks were more separated, partly because of ohmic potential drops. At both concentrations, the current and mass responses to fast ( $100 \text{ mV s}^{-1}$ )

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