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, metalorganic 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 size due to poor step coverage. Therefore, the improvement of bubbling technique has been studied to fill up contact or via holes in ULSI circuitry.

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 deposit carbon contamination at high rate. Therefore, the improvement of bubbler design or the development of performance additives 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 N2 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 1H 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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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.

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REFERENCES


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 di-anion > monoanion > solvent; salt does not participate. Solvent expulsion is faster than solvent entry. On short time scales during oxidation only di-anion motion responds to electron transfer.

Results and Discussion

Overview.—Figure 1 shows current (i) and mass responses to fast (100 ms) to a slow (5 ms) cyclic potential sweep for a PVF film in aqueous 8 and 250 mmol dm$^{-3}$ Na$_2$NDS solutions (in which PVF films are thermodynamically permselective, respectively) using methodology analogous to thermodynamic studies of this system. For the electrolytes and conditions used, PVF films are rigid, so the Sauerbrey equation applies. Cyclic voltammetric QCM experiments were carried out at 5 and 100 mv s$^{-1}$. The temperature was 23 ± 0.3 °C.

Experimental

The DQCM apparatus and its ability to compensate for changes in liquid-phase properties are described elsewhere. Closely matched 10 MHz AT-cut quartz crystals with evaporated Au electrodes were used. PVF films were deposited as before. Measurements were made in aqueous 8 and 250 mmol dm$^{-3}$ Na$_2$NDS solutions (in which PVF films are thermodynamically permselective and nonpermselective, respectively) using methodology analogous to thermodynamic studies of this system. 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 mv s$^{-1}$. The temperature was 23 ± 0.3 °C.

Results and Discussion

Overview.—Figure 1 shows current (i) and mass responses (ΔM) to a slow (5 ms) cyclic potential sweep for a PVF film in 250 mmol dm$^{-3}$ Na$_2$NDS. They are typical of PVF responses in aqueous media. Analogous data in 8 mmol dm$^{-3}$ Na$_2$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 ms)