Solubility of Several Short-Chain Lithium Dialkyldithiocarbamates in Liquid and Supercritical Carbon Dioxide

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The solubility of lithium diethyldithiocarbamate, lithium dipropyldithiocarbamate, lithium dibutyldithiocarbamate, and lithium bis(trifluoroethyl)dithiocarbamate was measured in liquid and supercritical carbon dioxide at (298, 308, and 318) K and at pressures between (80 and 250) bar. The solubilites were measured experimentally through traditional cloud point observations using a variable-volume stirred vessel with a sapphire window for visual inspection of the contents. These four short-chain lithium dialkyldithiocarbamates showed an increase in solubility with increasing density (or pressure) at fixed temperature. This increase was fairly independent of the temperature. Solubilites also increased with increasing temperature. The data were accurately modeled using an equation derived from association laws, which had a strong solvent density and temperature dependence.

Introduction

The generalized production of integrated circuits[1] is a multistep process in which the interlayer dielectric is etched into trenches and vias through lithographic processes. A barrier layer is added, and then void-free interconnect filling in the vias and trenches is typically accomplished using electrochemical deposition. This gives a nonuniform conductive coating, with superfilling of metal above the vias.[2] To successfully build the required multilevel metal interconnect structures, the metallic overburden must be removed and the conductor/SiO_2 surface planarized before the next level of interconnect can be added. Recently, copper has received much attention as an interconnect for computer chip manufacturing since it has greater electromigration resistance and higher current density than traditional interconnects.[3−7]

Although copper's properties are outstanding, there exist several major challenges to its implementation[8] including the fact that conventional dry-etch techniques to remove the overburden are not adequate.[9] Solution-based techniques to remove the overburden are commonly conducted in an aqueous slurry media; however, the porous low-dielectric inorganic and organic interlayer dielectric materials in the circuit are highly incompatible with water. Water removal is an extremely energy intensive and costly process. Inefficient water removal can result in higher than expected dielectric constants and an increase in interconnect defects during the manufacturing process. Water also has a high surface tension and viscosity that can collapse, by capillary action, the exquisitely fine (high aspect ratio) structures of the interconnect trenches and vias. The water used in interconnect manufacturing must be of ultrahigh purity as suspended particulates or dissolved ions or compounds can contaminate the wafer surfaces causing shorting or unwanted conductive pathways. It is estimated that over 32 000 g of wastewater along with 72 g of various other chemicals are required to produce a 2 g microchip.[10] Organic slurries are equally troublesome as they often include halogenated species such as chloroform or carbon tetrachloride.

Instead of using water or traditional organic solvents, we plan to use liquid and supercritical carbon dioxide as the solvent for copper overburden removal in a chemical mechanical planarization (CMP) process. Carbon dioxide has low viscosity, has high diffusivity, and can easily be reused in the CMP processes by reducing the pressure to remove the impurities. Liquid carbon dioxide has a very low surface tension. It is also inexpensive, environmentally friendly, and will not oxidize to produce impurities during the process. We have recently explored the use of various β-diketones[11,12] and bis(acetylacetone)ethylenediimine ligands[13] for copper removal in carbon dioxide. We have also used the lithium dialkyldithiocarbamates studied in this paper for copper removal[14] and have found them to have removal rates on the order of 250 monolayers/min, which is comparable to the currently required removal rates of 100 monolayers/min observed in industrial protocols. In this paper, we are not reporting the results of our CMP studies, but rather the solubilities of several short-chain lithium dialkyldithiocarbamates in liquid and supercritical carbon dioxide. These solubilities are critical for the scale-up, condition selection, design, and implementation of carbon dioxide-based CMP processes.

Several other investigators have explored the use of several other dithiocarbmates in carbon dioxide for metal removal, separation, and solubilite studies,[15−24] and some have used organic cosolvents to enhance solubilites.[25,26] However, organic cosolvents have the potential to contaminate copper interconnects, and we wish to avoid their use. Interestingly, none of the studies found in the literature explored the solubilites of short-chained lithium dialkyldithiocarbamates or their use in copper CMP removal. Short-chain dithiocarbamates with small counterions (such as lithium) are advantageous as they do not easily decom-

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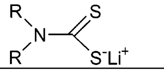
Table 1. Names and Structures of Lithium Dialkyldithiocarbamates Synthesized

R group		Abbreviation
ethyl (CH_3CH_2)	lithium diethyldithiocarbamate	Li EDDC
propyl ($CH_3CH_2CH_2$)	lithium dipropyldithiocarbamate	Li PDDC
butyl ($CH_3CH_2CH_2CH_2$)	lithium dibutyldithiocarbamate	Li BDDC
bis(trifluoroethyl) (CF_3CH_2)	lithium bis(trifluoroethyl)dithiocarbamate	Li FDDC

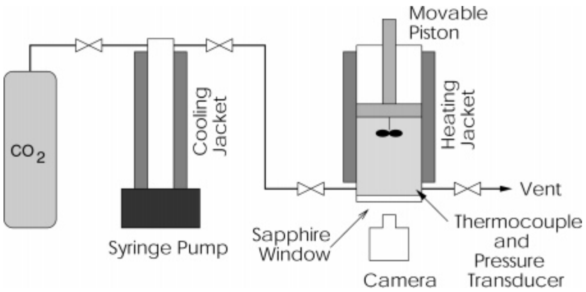


Figure 1. Phase equilibrium apparatus.

pose to produce bulky organic byproducts. Decomposition products have the potential to contaminate integrated circuits. The lithium dithiocarbamates are preferred as the larger sodium cations are much less soluble in condensed carbon dioxide media. It is important to note that the alkali metal counterion is necessary (i.e., lithium cannot be replaced with hydrogen) since the protonated forms of the dithiocarbamates are not stable and quickly decompose.[27]

Experimental Section

Materials. Research grade 5 carbon dioxide with a purity of 99.999 % was supplied by BOC Gases. Diethylamine, dipropylamine, dibutylamine, butyllithium (2.5 mol·L^{-1} in hexanes), diethyl ether, and carbon disulfide were supplied by Sigma-Aldrich. Bis(trifluoroethyl)amine was obtained from Synquest. All chemicals were used as received.

Lithium Dialkyldithiocarbamate Synthesis. In a typical synthesis, (0.013 to 0.017) mol of one of the amines was added to 10 mL of diethyl ether in a 100 mL round-bottom flask with stir bar held in an acetone-dry ice bath. The flask was purged with nitrogen, and a molar equivalent of n-butyllithium was added slowly to the contents. After 1 h, carbon disulfide (molar equivalent) in 10 mL diethyl ether was slowly added via a dropping funnel, and the flask was placed in a water-ice bath and then allowed to warm to room temperature overnight. The solution was reduced by rotary evaporation to about half the initial volume, vacuum filtered, and then purified via recrystallization or a silica gel column (methylene chloride eluent). Details of the synthesis, purification, and characterization of the lithium diakyldithiocarbamate (Li DDC) products (shown in Table 1) are presented elsewhere.[14]

Solubility Measurements. Solubilites of each lithium dialkyldithiocarbamate were found through cloud point measurements using a system manufactured by Thar Design Technologies (PEA-30ML phase equilibrium analyzer shown in Figure 1). We have successfully used this system to match the solubilities of ketoprofen found in the literature,[28,29] and we have measured the solubilites of several anesthetics[29] and β-adrenergic blocking agents[30] in liquid and supercritical carbon dioxide previously.

The PEA vessel contained a stirrer, a sapphire window to observe the cloud point, a heating jacket, and a movable piston that could change the PEA volume between (5.5 and 30) mL. A syringe pump (cooled to 5 °C) was used to deliver a fixed and controllable pressure of carbon dioxide to the PEA vessel. The PEA vessel's temperature (± 0.2 K) was monitored by a type K thermocouple, and pressure was measured by a Honeywell pressure transducer (± 0.1 %).

For an experimental solubility measurement, the PEA vessel was preheated to the desired temperature using a recirculating bath. The vessel was flushed with low pressure carbon dioxide, and a small amount of solid was weighed with an analytical balance, placed in the bottom of the vessel, and sealed. More low pressure carbon dioxide was purged through the vessel, which was then set to the smallest volume (5.5 mL) by moving the piston via a computer interface. The vessel was pressurized to the desired set point, and stirring was initiated. Once the desired pressure was obtained, the pressure was held constant by the syringe pump (within 0.5 bar) while the vessel volume was increased by raising the piston slowly until all solid was observed to dissolve. The vessel was then isolated from the pump via a valve, and the volume of the vessel was increased slowly until the cloud point was observed (the point at which material dropped out of solution). At the cloud point, the vessel volume, temperature, and pressure were recorded. The solubility was then calculated using the known amount of solid loaded into the vessel along with the amount of carbon dioxide present in the vessel, which was calculated from the known volume, temperature, and pressure using the NIST[31] tables for carbon dioxide. The vessel was then vented, cleaned with ethanol and acetone, and thoroughly dried prior to the next measurement.

Results and Discussion

The solubility mole fractions of the four lithium dialkyldithiocarbamates in liquid and supercritical carbon dioxide are shown in Tables 2−5 and Figures 2−5 (the dashed lines in these four figures are just linear fits of the data to assist the reader in observing trends, and they are not accurate models of the data). Solubilites were on the order of 10^{-5} to 10^{-4} mole fraction and increased with increasing density (and hence pressure) of carbon dioxide. These relatively low mole fractions were expected because of the ionic nature of the Li DDCs. However, even with low solubilites, copper removal rates with these compounds in carbon dioxide were faster than current industrial protocols.[14]

Some unique observations can be made concerning the solubility trends. First of all, the solubility of Li PDDC (with an odd number of carbons in the R group) is significantly lower than the solubility of both the Li EDDC and the Li BDDC (both with an even number of carbons in the R group). Since the alkyl groups are short, no significant difference in solubility would be expected based only on their length since longer chain lengths are generally required to see significant effects on solubility.[32] The two R groups attached to the nitrogen atom, however, do have the ability to twist and form different orientations when in solution. There might be some orientation with even chain lengths that place the methylene and methyl groups in a favorable orientation to enhance solubility. Several others investigators[33−36] have also ob-

Table 2. Mole Fraction Solubility (y) of Li EDDC in Liquid and Supercritical Carbon Dioxide

T = 298 K			T = 308 K			T = 318 K		
P/bar	ρ/g·cm^{-3}	$y \times 10^5$	P/bar	ρ/g·cm^{-3}	$y \times 10^5$	P/bar	ρ/g·cm^{-3}	$y \times 10^5$
85	0.79	0.026	100	0.72	1.65	125	0.68	2.04
100	0.82	1.02	125	0.78	3.61	150	0.74	5.60
125	0.85	1.97	150	0.82	3.92	175	0.78	8.83
150	0.88	2.91	175	0.84	5.36	187	0.80	11.46
175	0.90	3.65	200	0.87	5.97	200	0.81	12.70
200	0.92	4.09	225	0.89	6.96	225	0.84	16.47
225	0.93	4.46	250	0.90	10.02			
250	0.94	5.84						

Table 3. Mole Fraction Solubility (y) of Li PDDC in Liquid and Supercritical Carbon Dioxide

T = 298 K			T = 308 K			T = 318 K		
P/bar	ρ/g·cm^{-3}	$y \times 10^5$	P/bar	ρ/g·cm^{-3}	$y \times 10^5$	P/bar	ρ/g·cm^{-3}	$y \times 10^5$
122	0.85	0.05	100	0.71	0.056	121	0.66	0.20
151	0.88	0.25	125	0.78	0.23	152	0.75	1.02
175	0.90	0.55	150	0.82	0.59	175	0.78	1.97
200	0.92	0.75	175	0.84	0.90	200	0.81	2.33
225	0.93	1.17	200	0.87	1.87	225	0.84	2.74
237	0.94	1.37	225	0.89	2.10	237	0.85	3.15
250	0.94	1.99	237	0.89	2.42	250	0.86	4.00
			250	0.90	2.60			

Table 4. Mole Fraction Solubility (y) of Li BDDC in Liquid and Supercritical Carbon Dioxide

T = 298 K			T = 308 K			T = 318 K		
P/bar	ρ/g·cm^{-3}	$y \times 10^5$	P/bar	ρ/g·cm^{-3}	$y \times 10^5$	P/bar	ρ/g·cm^{-3}	$y \times 10^5$
80	0.78	2.57	85	0.61	3.90	81	0.25	9.23
89	0.80	3.15	99	0.71	5.22	90	0.34	10.29
99	0.82	3.94	125	0.78	6.98	100	0.50	10.56
124	0.85	4.80	149	0.81	8.19	124	0.67	12.64
149	0.88	5.74	175	0.84	10.29	149	0.74	14.33
174	0.90	7.48	199	0.86	10.84	174	0.78	14.26
199	0.91	8.34	224	0.88	12.35	199	0.81	14.90
224	0.93	9.16	249	0.90	14.37	224	0.84	15.24
248	0.94	11.34				249	0.86	16.89

Table 5. Mole Fraction Solubility (y) of Li FDDC in Liquid and Supercritical Carbon Dioxide

T = 298 K			T = 308 K			T = 318 K		
P/bar	ρ/g·cm^{-3}	$y \times 10^5$	P/bar	ρ/g·cm^{-3}	$y \times 10^5$	P/bar	ρ/g·cm^{-3}	$y \times 10^5$
99	0.82	2.57	99	0.71	3.15	99	0.48	1.73
124	0.85	3.41	99	0.71	3.22	124	0.67	3.64
149	0.88	3.68	124	0.77	3.96	149	0.74	4.45
173	0.90	5.13	149	0.81	4.29	173	0.78	5.29
199	0.91	5.13	173	0.84	5.35	199	0.81	5.81
224	0.93	5.66	199	0.86	5.69	224	0.84	5.94
248	0.94	6.47	224	0.88	5.79	248	0.86	6.86
			249	0.90	6.08			
			249	0.90	6.18			

served some changes in solubilities for odd versus even chain lengths.

The Li FDDC (Figure 5) solubility also showed some interesting results when compared to its unfluorinated analogue, Li EDDC (Figure 2). Adding fluorinated functional groups to compounds tends to increase their solubility in carbon dioxide.[37−41] However, to show significant solubility increases, a large number of carbons usually need to be fully fluorinated. We were only able to fluorinate one carbon on the ethyl functional group due to the availability of starting amines. This low level of fluorination had minimal effect on the solubility. At low temperatures, it appeared the Li FDDC had a slightly increased solubility over Li EDDC. At higher temperatures, the Li FDDC tended to have a lower solubility.

By examining Figures 2−5, it is clear that both density and temperature have a strong influence on the solubilities of the lithium dialkyldithiocarbamates in liquid and supercritical carbon dioxide. As both density and temperature are increased, the solubility increases. It would be difficult to model the solubilites using a traditional equation of state-fugacity approach. First of all, equation of state parameters, while known for pure carbon dioxide, are not available for the lithium dialkydithiocarbamamtes. The critical properties, acentric factor, and other properties of the lithium dialkydithiocarbamates are not available, nor are they easily measured since the compounds decompose before they reach a critical temperature. Estimation techniques, such as models based upon group contribution theory, have not been worked out for these unique ionic compounds. Furthermore, sublimation pressures of the solids would be required as a function of temperature to accurately use the equation of state-fugacity approach to model and predict solubilites, and again this property for the pure lithium dialkydithiocarbamates is not available or easily predicted. Instead of using a rigorous equation of state-based model, we examined the available literature for models that showed heavy dependence on both the density and the temperature of carbon dioxide. The model also needed to have a density dependence that was able to

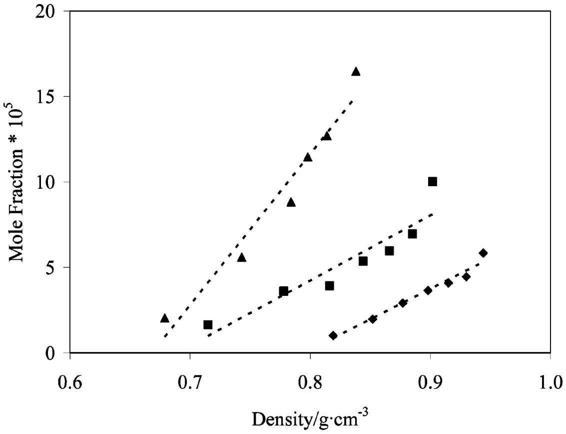


Figure 2. Mole fraction solubility of Li EDDC in liquid and supercritical carbon dioxide as a function of density. ◆, 298 K; ■, 308 K; ▲, 318 K.

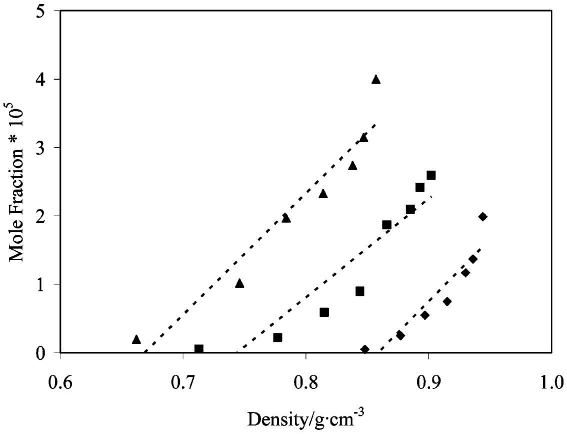


Figure 3. Mole fraction solubility of Li PDDC in liquid and supercritical carbon dioxide as a function of density. ◆, 298 K; ■, 308 K; ▲, 318 K.

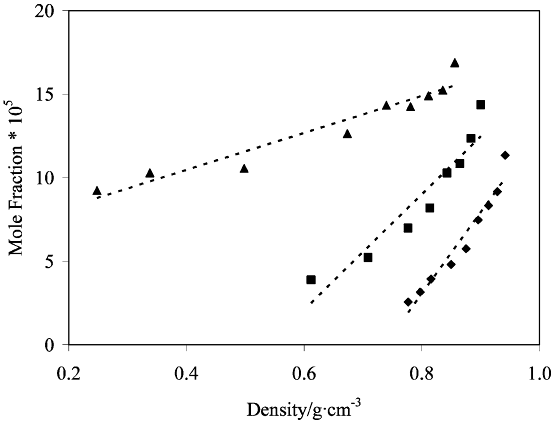


Figure 4. Mole fraction solubility of Li BDDC in liquid and supercritical carbon dioxide as a function of density. ◆, 298 K; ■, 308 K; ▲, 318 K.

vary independent of the temperature since the slopes of straight lines in Figures 2−5 changed with varying temperature. The model derived from the association laws of Chrastil[42] met all of our requirements.

Chrastil's model is based on the assumption that when a molecule of lithium dialkyldithiocarbamate dissolves into dense carbon dioxide a specific number of carbon dioxide molecules (k) associate closely with the solvated molecule forming a shell that has large interactions with the solvated molecule.[43] It is this solvated complex that is in equilibrium with the system rather than pure solid lithium dialkyldithiocarbamate in the carbon dioxide rich phase (see eq 1):

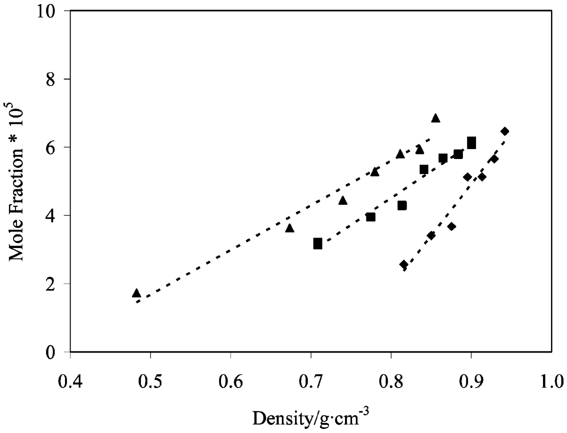


Figure 5. Mole fraction solubility of Li FDDC in liquid and supercritical carbon dioxide as a function of density. ◆, 298 K; ■, 308 K; ▲, 318 K.

Table 6. Fitted Model Parameters

lithium dialkyldithiocarbamate	k	a	b
Li EDDC	9.5	−10,699	−31.3
Li PDDC	12.7	−9,895	−56.7
Li BDDC	5.2	−5,023	−19.8
Li FDDC	4.3	−2,409	−22.2

$$\mathrm{DDC} + k\mathrm{CO_2} \rightleftarrows \mathrm{DDC{\cdot}CO_{2_k}} \tag{1}$$

The association number (k) is not expected to be an integer as, in many cases, the solvated complexes are not stoichiometric.[42]

It is possible to derive equilibrium expressions from the mechanism shown in eq 1 (see Chrastil's original work[42] for the details) to derive a final expression shown in eq 2:

$$c/\mathrm{g{\cdot}L^{-1}} = (\rho/\mathrm{g{\cdot}L^{-1}})^k \exp\left(\frac{a}{T/\mathrm{K}} + b\right) \tag{2}$$

where c is the concentration of Li DDC in carbon dioxide, ρ is the density of carbon dioxide, k is the association number, T is the temperature, and a and b are constants. The two constants, a and b, have physical significance shown in eqs 3 and 4, respectively:

$$a = \frac{-\Delta H}{R}$$

$$b = \ln(M_{\mathrm{DDC}} + M_{\mathrm{CO_2}}) + q - k\ln(M_{\mathrm{CO_2}}) \tag{4}$$

where ΔH is the enthalpy change of solvation and phase change combined, R is the universal gas constant, M_i is the molecular weight of species i, and q is an integration constant when the Clausius equation was applied and has some dependence upon the melting points of the solute and solvent.[43] The fitted (by least-squares method) model parameters for the four lithium dialkyldithiocarbamates are presented in Table 6. A parity plot for the model is shown in Figure 6, which reveals a relatively good fit of the data.

The enthalpy of solvation (expressed by the a constant) tended to become less negative with increasing alkyl chain length. It also increased significantly when the alkyl substituent was partially fluorinated. The association number (k) tended to decrease with increasing chain length

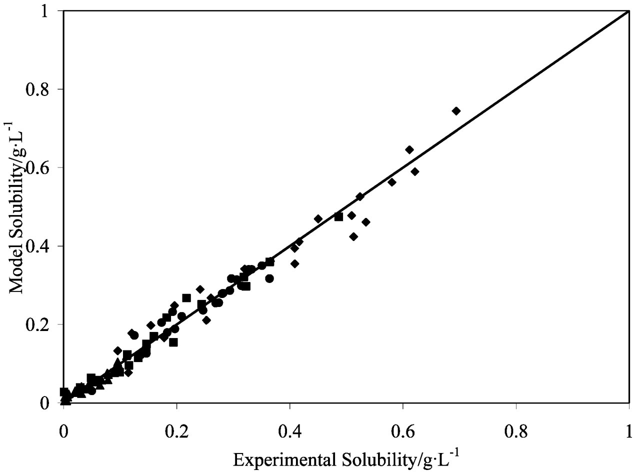


Figure 6. Parity plot of solubility data. ■, ethyl; ▲, propyl; ◆, butyl; ●, bis(trifluoroethyl).

(with the exception of the Li PDDC) and fluorination. As we have previously discussed, the Li PDDC is thought to interact differently with carbon dioxide, possibly forming a different orientation, than the other compounds explored in this study.

Conclusions

The solubilities of these four short-chain dialkyldithiocarbamates were high enough to be effective chelating agents for the removal of copper in liquid and supercritical carbon dioxide. A simple association model with temperature and solvent density dependence accurately captured the solubility data and can be used for the design of a carbon dioxide based CMP process. Solubilities increased with increasing density and temperature.

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