Complexing Agents (CAs) for Semiconductor Cleaning Chemistries: Characterization of CA Lifetimes by UV/VIS-Spectroscopy

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In recent years there has been a trend to improve the conventional RCA cleaning sequence. This is mainly a consequence of the progress in device integration coupled with the demand for a greater reduction of organic, particle and metallic surface contamination. A novel approach in wet cleaning is the single chemistry cleaning referred to as APM+ (1, 2, 3, 4): this consists of an alkaline cleaning solution spiked with a complexing agent (CA) and combines the SC1 and SC2 cleaning features. Since the CAs employed are organic compounds, knowledge of their lifetimes in strongly oxidizing media is of considerable significance and may be determined by means of UV/VIS-spectroscopy. However, this method is limited to CAs bearing a chromophoric group, that is to say, conventionally applied CAs like EDTA and Dequest 2060s are not directly accessible.

The present trials were run with a set of well-known CAs which are exclusively aromatic ligands: pyridinones (5), catechol, 8hqsa (see fig. 1) and *'X'*. Cleaning solutions of 1/4/20 APM and 1.65/1/5 NC (with 2% choline replacing ammonia), each with ~ 3.2 mM of a CA added, were prepared and maintained at 35°C and 50°C. From these mixtures, aliquots were collected roughly every five minutes to study the decomposition of the CAs. The collected samples were immediately frozen in liquid nitrogen. The UV/VIS absorption measurements of the defrosted samples were performed against a reference cell with an aliquot of freshly prepared cleaning solution in order to eliminate substantial peroxide absorption. Both the sample and the reference were taken up in a buffer solution of pH 9.5.

The absorptions were converted to "total concentrations" i.e. the sum of all protonated and deprotonated species in solution, normalized and plotted against the sampling time. Regression curves representing a linear or an exponential decay were then calculated and stand for rate equations of zeroth- and first- or pseudo-first-order, respectively. The reaction half-lifetimes ($t_{1/2}$) were deduced from calculated parameters. Figure 2 shows a so-called "difference equation" graph: the absorbance of ESEHP at the moment t is plotted against the absorbances at t+Δ, whereby Δ is in the order of the half-lifetime of the reaction observed and the decay of absorbance is assumed to follow a first-order reaction. The conditions for a first order reaction are given when the points plotted lie on a straight line passing through the origin. Table I gives an overview of the half-lifetimes determined. It is obvious that the lifetimes of the CAs are higher in NC than in APM and, as expected, are also prolonged if the bath temperature is reduced.

References

1. M. Bayens, W. Hub, B. O. Kolbesen, A. R. Martin, P. W. Mertens, Solid State Phenomena Vol. 65-66, 23-26 *(4th Ultra Clean Processing of Silicon Surfaces, 1998)*
2. R. Vos, O. Doll, A. Fester, B. O. Kolbesen, M. Lux, K. Kenis, B. Onsia, S. Degendt, E. Schellekes, Z. Hatcher, P. Mertens, M. Heyns, Diffusion and Defect Data - Solid State Data, Pt B: Solid State Phenomena Vol. 76-77, 119-122 *(5th Ultra Clean Processing of Silicon Surfaces, 2000*)
3. B. Onsia, E. Schellkes, R. Vos, S. De Gendt, O. Doll, A. Fester, B. Kolbesen, M. Hoffman, Z. Hatcher, K. Wolke, P. Mertens, M. Heyns, in Cleaning technology in Semiconductor Device Manufacturing VII, J. Ruzyllo, R. Novak, T. Hatrori, R. Opila, Editors, p. 23, The Electrochemical Society Proceeding Series, Pennington, NJ (2001)
4. R. Vos, M. Lux, K. Kenis, M. Maes, B. Onsia, J. Snow, F. Holsteyn, G. Vereecke, P. W. Mertens, M. M. Heyns, O. Doll, A. Fester, B. O. Kolbesen, T. Hackett, M. Hoffman, *Single Chemistry Cleaning Solutions for Advanced Wafer Cleaning*, to be published *(6th Ultra CleanProcessing of Silicon Surfaces, 2002)*
5. R. Vos, P. W. Mertens. A. Fester, O. Doll, B. O. Kolbesen, PCT patent, WO 02/051961 A2

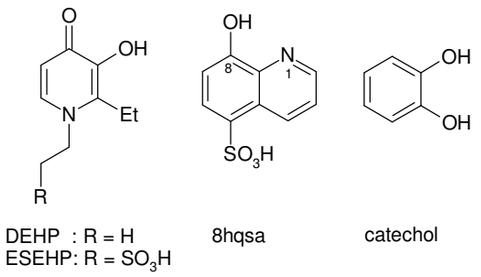

Figure 1: Structures of CAs employed in this study.

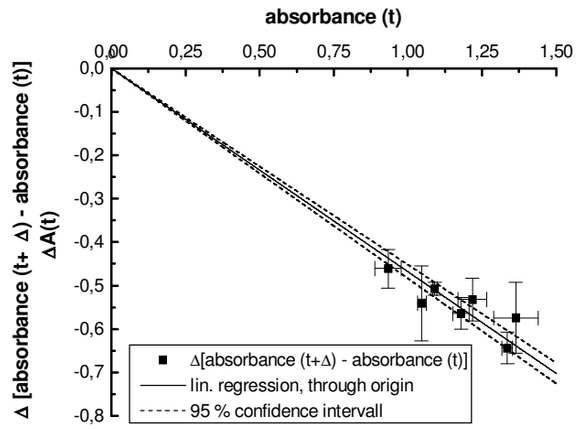

Figure 2: So-called "difference equation" plot of CA ESEHP.

Table I: Half-lifetimes of the CAs investigated, deduced from their regression parameters

medium	T [°C]	CA	half-lifetimes [min] $t_{1/2}$	
1/4/20 APM	35	DEHP	212	
1/4/20 APM	50	DEHP	60/70	
1.65/1/5 NC	35	DEHP	268	
1.65/1/5 NC	50	DEHP	78/73	
1/4/20 APM	50	ESEHP	66	
			linear	exponential
1/4/20 APM	50	**X**	230/251	575/310
1/4/20 APM	50	catechol	53	51
1/4/20 APM	50	8hqsa	85	81