Alicyclic Polymers Based on t-BOC Norbornene Derivatives and Maleic Anhydride for Applications as ArF Photoresists

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The ArF excimer laser lithography is venerable practical technology for gigabit ICs fabrication employing the design rule under 0.15 μmresolution.[1] The single-layer positive photoresist materials for 193 nmmicrolithography should provide the requisite properties such as high sensitivity and transparency at the 193 nmexposure wavelength, and most importantly high plasma-etch resistance.[2] The high sensitivity can be realized through chemical amplification by acid-catalyzed reactions using acid-labile polymers. Two key requirements, transparency at 193 nmand etch resistance, were once considered to be mutually exclusive for incorporation into a single polymer chain structure. The major research efforts have been continued over the last several years to fulfil the requirements and have led to the development of alicyclic (or cycloaliphatic) polymers having alicyclic, plasma etch-resistant moieties in the side-chains or backbones.[3]

Current research efforts have focused on main-chain alicyclic polymers based on norbornene (NB) monomers because such alicyclic structures provide effective plasma-etch resistance as well as high transparency at 193 nmThe predesigned alicyclic polymers have been successfully obtained by electron donor/acceptor (EDA) radical polymerizations utilizing norbornene derivatives as an electron-donor monomer and maleic anhydride (MAh) as an electron-acceptor monomer.[4,5] Even further inclusion of alicyclic moieties was accomplished using multi-carbocyclic compounds such as tricyclodecyl or tetracyclodecyl side-chain mthacrylates and tetracyclodecene monomers.[6] A great number of alicyclic polymers based on 5-norbornene derivatives with polar-substituents at 2-position, most importantly, an acid-cleavable *tert*-butyloxycarbonyl (t-BOC) group were investigated as ArF photoresists. The t-BOC monomer, namely, *t*-butyl bicyclo[2.2.1]hept-5-ene-2-carboxylate or 2-t-BOC-5-norbornene [t-BOCNB], have been radically co- and ter- or quater-polymerized with other NB-derivatives [RfNB] and MAh by EDA polymerization to make acid-labile t-BOC protected alicyclic polymers.[7] Recently, some detailed properties of new series of alicyclic polymers based on t-BOCNB were disclosed for successful applications as chemically amplified, single layer, positive-tone photoresists in 193nm lithography.[8].