are associated with the α process in the following manner: The 240K loss process ($R1$) results from a fast chain motion of short correlation length along the chain. The 310K loss process ($R2$) results from a slower motion of longer correlation length at low temperatures. Thus in low frequency dielectric measurements $R2$ dominates and determines the location of the 'α loss' maximum. At higher temperatures the degree of cooperativity required for motion decreases and $R2$ loses strength. However, $R1$ couples strongly to high frequency phonons, thus reversing the relative strengths of the two processes. We are to undertake a careful dielectric study of PDMS at temperatures below T_α to investigate this possibility. Though conjectural in this case, recent work[6] indicates just such a process in poly(4-chlorostyrene). Careful analysis of low frequency (up to a few kHz) data indicates a weak but distinct fast process comprising about 2% of the total dielectric relaxation strength. Plotted on a transition map the fast process data may be extrapolated to meet the point obtained from hypersonic measurements ($\sim$10 GHz) and assigned to the β relaxation[5], whilst the slower process data indicates that another hypersonic loss maximum may be found at substantially higher temperatures. The 'fast process' data is quite distinct from the so-called β process which occurs at substantially lower temperatures and is characterized by a lower activation energy at these low frequencies. Another difficulty is presented by the relatively strong effect of crosslinking on the hypersonic properties of the rubber even at fairly low crosslink densities[1]. This behaviour contrasts with the small effects seen in model polyurethane networks[7], and it is tempting to account for it in terms of structural scattering (see for example the data of Bedborough and Jackson[8]) associated with crosslink induced structure. However, the similarity of the strength of the 240K process in the fluid and network would seem to preclude this explanation. However, our rubber samples were prepared by radiation crosslinking, and undoubtedly contain small bubbles which may induce local structure[9]. There is also some evidence for a significant number of short chain lengths in these networks[10]. Their presence might influence the hypersonic loss data considerably. Model networks of PDMS are now available[11] and experiments with these materials may clarify the origin of the hypersonic loss we observe at low crosslink densities[1].

In conclusion we report these measurements not only because they confirm our suspicions about the inadequacy of our original model, but also because they cast doubt on earlier rather simple interpretations of the hypersonic loss process. We await the outcome of the experiments referred to for further clarification.

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Electron resists prepared from colloidal dispersions of poly(methyl methacrylate) in non-solvents

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Introduction

Electron-beam lithography has become an important technique in the fabrication of microelectronic devices[1,2]. Its use stems from the fact that it can produce line widths which are an order of magnitude smaller than those available from the best photolithographic processes. Poly(methyl methacrylate), (PMMA), has been widely used as a resist in electron-beam lithography[3,4]. The substrate to be pattern-delineated is usually first covered with a polymer film by spin-coating PMMA from a molecular solution in a good solvent. The system is selectively irradiated by a focused beam of electrons and in what amounts to a developing process the degraded polymer is removed with the aid of a selective solvent to form a positive image. The usefulness of a polymer as a resist depends on its film forming and adhesive properties, sensitivity to electron irradiation, resolution and chemical resistance to etching solutions. Sensitivity for a given film thickness is usually defined as the minimum electrical charge per unit area of resist film required for complete development of the exposed area. Resolution is usually given as the minimum linewidth that can be developed in the resist layer; it is very much dependent on the resist thickness, the line spacing, the accelerating voltage and the nature of the substrate[5]. There are a number of polymers, e.g. poly(butene-1-sulphone), which are considerably more sensitive as electron resist than PMMA[6]. The latter is still extensively used, however, in fabrication

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processes because of its merits with regard to the other required properties.

In this communication we show that films spin-cast from colloidal dispersions of PMMA in a hydrocarbon are significantly more sensitive as electron resists than films formed in the conventional manner from PMMA solutions.

Experimental

Two dispersions were used in the study. The first was prepared by polymerizing methyl methacrylate monomer with a free radical initiator in the presence of a polystyrene–poly(ethylene/propylene) block copolymer. The latter acted as a stabilizing agent and during and after polymerization in heptane held particles of PMMA in colloidal suspension. The particles, each of which contained many polymer chains, had a number-average particle diameter, $\bar{D}_n$, of 0.3 μm, and the individual polymer chains had a number-average molecular weight, $\bar{M}_n$, of 210 000 and weight-average molecular weight, $\bar{M}_w$, of 508 000. The second dispersion was kindly supplied by ICI Paints Division, Slough. In this case the non-solvent was iso-octane and the stabilizing agent was a graft copolymer consisting of a poly(methyl methacrylate) backbone and poly(12-hydroxystearic acid) grafts. For these particles $\bar{D}_n = 0.2$ μm and for individual chains $\bar{M}_n = 67\,000$ and $\bar{M}_w = 292\,000$. The dispersions were compared with two solutions of PMMA in methyl isobutyl ketone (MIBK). The first was prepared from a sample supplied by BDH ($\bar{M}_w = 188\,700$, $\bar{M}_w/\bar{M}_n = 2.28$) and the second from a sample of Du Pont's Elvacite 2041 ($\bar{M}_w = 457\,000$, $\bar{M}_w/\bar{M}_n = 2.96$).

The dispersions and solutions were deposited onto a chromium/glass substrate by the flood technique, and spun at high speed to produce a resist thickness of 5000 Å. The thickness of the chromium was 350 nm. Specimens of dispersion-based resists were baked on a hot plate for 20 min at 130°C whilst specimens of solution based resists had to be maintained at 170°C for 30 min, to remove all the residual solvent and release spinning strains. The polymeric resists were then tested with a beam of energy 20 kV and a width of 0.25 μm. The beam current was measured, by a Faraday cage, before and after each series of exposure patterns. Each exposure pattern consisted of a series of subpatterns built up from an array of spots. For each series of patterns within the overall exposure pattern the spot exposure time was varied from 4 to 998 μs. A resolution test pattern was also included with each exposure pattern.

The developing cycle, which followed the exposure of the resist, consisted of (i) a 2 min soak, (ii) a 30 s spray with developer followed by (iii) a 2 min soak, (iv) a 30 s spray in isopropyl alcohol, (IPA), to remove all traces of the developer. The developer used was a 3:1 mixture of IPA and MIBK, except for dispersion 1 which gave better results with a 9:4 mixture of IPA to cyclohexanone. After development the specimens were then baked for 30 min at 130°C to reduce undercutting except for dispersion 1 which did not need this treatment. The chromium was then etched by an acidic ceric sulphate solution and finally the resists were removed by soaking in acetone.

Table 1 Sensitivities of the systems studied

Polymer	Sensitivity (C m^{-2})
Dispersion 1	0.31–0.35
Dispersion 2	0.28–0.38
BDH poly(methyl methacrylate)	0.86–1.04
Elvacite poly(methyl methacrylate)	0.89–0.99

Results

The measured sensitivities of the various systems studied are recorded in *Table* 1. In each case the film thickness was 0.5 μm. The enhanced sensitivity of the dispersion-based films is tentatively attributed to lack of any strong adhesion between neighbouring particles. We believe that when a significant fraction of chains within a particle have been degraded, the particle can easily be dislodged and washed out by the solvent. In the case of solution cast films the chains are uniformly entangled throughout the film and not subject to the same development mechanism.

The electron beam we used in the investigation was too broad to enable measurements to be made of the limiting linewidths which could be obtained from the systems. In future studies we hope to carry out tests with a finer beam. In general, however, resolution patterns produced in the present work from dispersion-spun resists had equally good or better definition than those produced from solution-spun resists. In order to obtain the highest possible resolution from the dispersion systems it will be necessary to use colloidal particles with diameters < 1000 Å. Synthetic work is presently underway in our laboratory to produce such systems.

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