Thin Solid Films 539 (2013) 274–277

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Synthesis and electrical characterization of low-temperature thermal-cured epoxy resin/functionalized silica hybrid-thin films for application as gate dielectrics

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ARTICLE INFO

Article history:
Received 14 September 2012
Received in revised form 30 April 2013
Accepted 1 May 2013
Available online 17 May 2013

Keywords:
Gate dielectrics
Silica
Epoxy resin
Hybrid
Thin film

ABSTRACT

Thermal-cured hybrid materials were synthesized from homogenous hybrid sols of epoxy resins and organoalkoxysilane-functionalized silica. The chemical structures of raw materials and obtained hybrid materials were characterized using Fourier transform infrared spectroscopy. The thermal resistance of the hybrids was enhanced by hybridization. The interaction between epoxy matrix and the silica particles, which caused hydrogen bonding and van der Waals force was strengthened by organoalkoxysilane. The degradation temperature of the hybrids was improved by approximately 30 °C over that of the parent epoxy material. The hybrid materials were formed into uniformly coated thin films of about 50 nm-thick using a spin coater. An optimum mixing ratio was used to form smooth-surfaced hybrid films. The electrical property of the hybrid film was characterized, and the leakage current was found to be well below 10^{-6} A cm^{-2}.

1. Introduction

Many research efforts have recently focused on improving the thermal stability and increasing the dimensional stability of epoxy resins because epoxy resins have excellent adhesion, chemical resistance, and electrical insulation properties [1,2]. However, it is difficult to form them into thin layers because of their high viscosities, which originally apply industrial adhesive or stationery glues. Efforts are constantly being made to achieve this objective in modern electronic and electrical applications [3,4]. Formation of hybrid materials with organic and inorganic compounds promises to improve the film-forming property and thermal stability. Silica, an inorganic material, is a promising candidate for enhancing the thermal and insulating properties of hybrid materials [5]. The formation of silica-based films requires that silica materials undergo further processing such as high-temperature heat treatment or hybridizing with other materials. Sol–gel reaction with organoalkoxysilane coupling agents is used to prepare the hybrid materials in order to enhance the inorganic-organic, i.e., silica-organoalkoxysilane, interfacial compatibility of the materials [6–8].

In this paper, we report the synthesis and characterization of a low-temperature thermal-curable hybrid material using epoxy resin and nanosized colloidal silica for application as gate dielectrics. The chemical structure and thermal stability of the synthesized hybrid materials were studied. The surface morphology and insulation property of hybrid films were investigated.

2. Experimental details

2.1. Materials

LUDOX® water-dispersed colloidal silica (diameter: 12 nm, silica content: 30 wt%) and the organoalkoxysilanes, methyltrimethoxysilane (MTMS) and phenyltrimethoxysilane (PTMS) were obtained from Sigma-Aldrich Co. The epoxy resin was prepared using trikis (glycidyloxyphenyl) methane (TGPM) and of (3,4-epoxycyclohexane) methyl 3′–4′-epoxycyclohexyl-carboxylate (ECMECC) (molecular weight: 369.34 g/mol; epoxy number: 7.33; viscosity: 4.28 cP at RT). The reagents used to prepare the epoxy resin were obtained from Kolon industries Inc. Methylbicyclo[2.2.1]heptane-2,3-dicarboxylic anhydride (MBHDA) (molecular weight: 180.0 g/mol; epoxy number: 8.89; viscosity: 7.24 cP at RT) was used as the curing agent, and 2-methylimidazole was used as the thermal-curing catalyst. The chemical structures of organoalkoxysilanes, the epoxy resin, and the curing agent are shown in Fig. 1.

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http://dx.doi.org/10.1016/j.tsf.2013.05.005

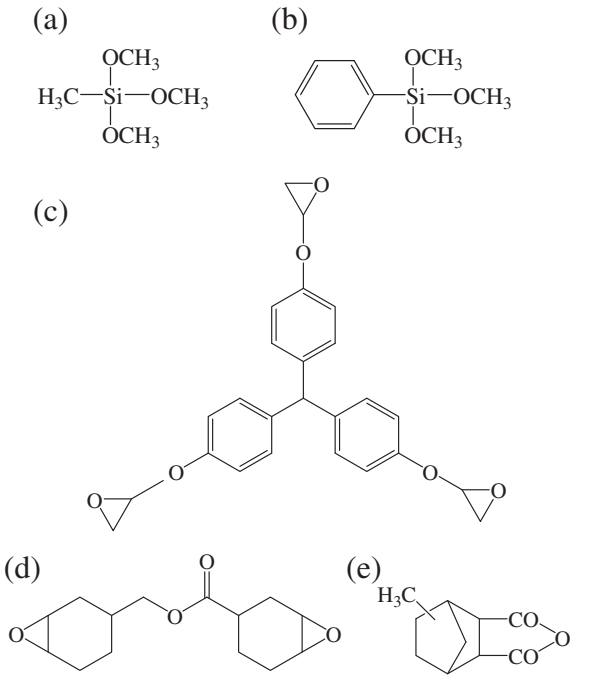

Fig. 1. Chemical structures of (a) methyltrimethoxysilane (MTMS), (b) phenyltrimethoxysilane (PTMS), (c) trikis(glycidyloxyphenyl) methane (TGPM), (d) (3,4-epoxycyclohexane) methyl 3′–4′-epoxycyclohexylcarboxylate (ECMECC), and (e) methylbicyclo [2.2.1] heptane-2,3-dicarboxylic anhydride (MBHDA).

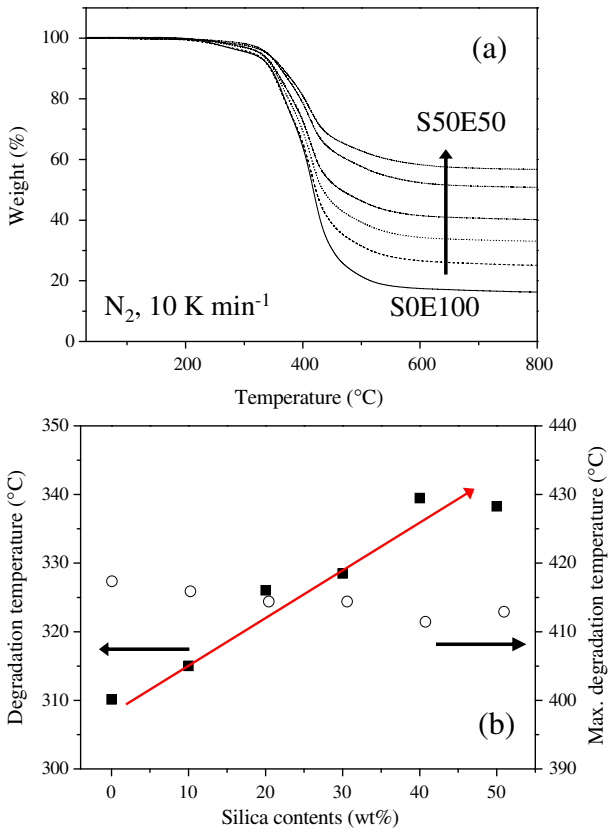

Fig. 3. (a) TGA thermograms of silica and organoalkoxysilane-functionalized silica. (b) Degradation temperature of hybrid sol for 5% weight loss and maximum degradation temperature with silica contents.

2.2. Synthesis of the materials

The water-dispersed silica was functionalized by continuous hydrolysis and condensation with the organoalkoxysilanes MTMS and PTMS using the sol–gel reaction. The epoxy resin was prepared from a mixture of 80 wt% TGPM and 20 wt% ECMECC. The epoxy/silica hybrids were synthesized with various specific weight ratios of the epoxy resin and the organoalkoxysilane-functionalized silica as follows: 0/100 (S0E100), 10/90 (S10E90), 20/80 (S20E80), 30/70 (S30E70), 40/60 (S40E60), and 50/50 (S50E50) (where S is the wt% of silica and E is the wt% of the epoxy resin). The hybrid solutions were stirred for 1 h and either dropped or spin-coated at 4000 rpm onto substrates. The specimens were pre-dried at 150 °C for 1 h and thermal-cured successively heating at 180 °C for 2 h.

2.3. Characterization of the materials

The structures of the hybrid materials were determined using Fourier transform infrared spectroscopy (FT-IR, JASCO FT-IR 4200). The thermal stabilities of the hybrid materials were measured at a heating rate of 10 K min^{-1} in a 100 mL min^{-1} N_2 flow using thermogravimetric analysis (TGA, TA instruments SDT Q600). The surface morphology of the coated hybrid films was observed using field-emission scanning electron microscopy (FE-SEM, Hitachi S48000) accelerating voltage at 10 kV and atomic force microscopy (AFM, VEECO DIMENSION 3100) operating in tapping mode. The metal–insulator–metal (MIM) structures were examined to determine the insulation properties of the

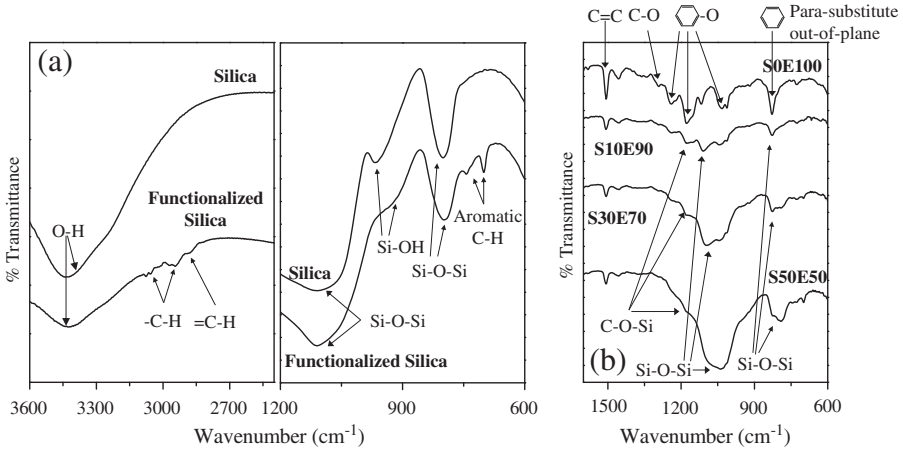

Fig. 2. FT-IR spectrum of (a) silica and organoalkoxysilane-functionalized silica and (b) mixed ratio hybrid materials after curing.