Effect of Spin Coating on the Curing Rate of Epoxy Adhesive for the Fabrication of a Polymer Optical Waveguide

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Spin coating is a simple process for rapidly depositing thin, solid polymeric films onto relatively flat substrates. Evaporation occurs during spinning of the relatively volatile species in any solution. The curing behavior of spin-coated polymeric film is influenced by the evaporation of any reactive component. An investigation was carried out on a silicon substrate to study the effects of spin coating on the curing behavior of the epoxy adhesive. The degree of curing for both spin and without spin-coated epoxy adhesive was measured by Fourier-transform infrared spectroscopy (FTIR). A slower curing reaction rate was observed for the spin-coated epoxy adhesive. The composition gradient established by solvent evaporation during spinning is responsible for the slower curing reaction rate of the spin-coated epoxy adhesive. From this study, it is proposed to use solvents that are less volatile and allow a greater part of the thinning behavior to occur without significant changes in the fluid properties during the spinning process.

Key words: Spin coating, epoxy, solvent evaporation, composition gradient, curing rate, Fourier transform infrared spectroscopy (FTIR)

INTRODUCTION

Polymeric adhesive as a cladding material is used for optical waveguides, offering integratable photonic devices, ease of processing, low cost, and high performance, and satisfying a significant industry need.1 The physical, optical, and thermomechanical properties of the cured adhesives depend on the degree of curing of the adhesive constituents.2 Ultraviolet (UV) curing is a process applied to polymerize the adhesives compounds to achieve the transition from liquid to solid as a result of their exposure to UV radiation. It is an attractive alternative to conventional curing because it offers several distinct advantages.

• It is a high-speed process.
• It operates at room temperature, so temperature-sensitive material can be coated.
• It has lower energy consumption because substrates and components need not be heated.3

Typical polymeric solutions are complex mixtures of solvents, stabilizers, surfactants, and precursor molecules that have been designed to optimize various coating characteristics.4 Reactive solvents have an important role in the UV curing of polymeric adhesives. The advantage of using reactive solvents is that both the processing temperature and viscosity can be lowered with respect to the polymer to be processed. In addition, there is no need for solvent removal after processing; the solvent becomes a useful structural part of the final system, depending on the proper reactive solvent (monomer).5

Thin polymer films can be deposited by a variety of techniques with different complexity and applicability. The choice of deposition technique depends upon the physicochemical properties of the material, the film quality requirements, and the substrate being coated. The final properties of these films also depend on their morphologies, which are largely affected by the polymer chain orientation and the state of aggregates. One of the simplest and most common techniques of applying thin films onto wafers is spin coating. This technique leads to very uniform films with well-controlled thickness.6 Because of the complexity of common spin-coating solutions, the behavior of mixed solutions should be
understood under the conditions of rapid fluid flow and convectively driven evaporation that occurs during spin coating. Many studies have been directed to predict final film properties, but no attempt has been paid to the changes in curing behavior induced by the spinning process.

The aims of this paper are to study and understand the effect of spin coating on the curing process of an epoxy adhesive. A better understanding of the effects of the spin coating on the polymer film curing is important in making high-quality thin film. Fourier-transform infrared spectroscopy (FTIR) was used to explore the curing rate of a UV-curable epoxy adhesive. The results of this study can allow manufacturers to develop a highly reliable and better performance polymer optical waveguide.

EXPERIMENTS

Sample Preparation

An epoxy-based, commercial UV-curable adhesive was used for this study. It is a clear, ultralow viscous, 100% reactive liquid that can be cured readily by exposing to UV light. The substrates used in the experiments were highly polished silicon wafers. Organic residues on the silicon-covered surfaces were removed by successive ultrasonic cleaning with acetone, alcohol, and deionized water. Through-out this investigation, 2 cm × 2 cm square-edge silicon wafers were used to avoid the radial nonsymmetry in rectangular substrates that causes larger corner build-up effects on the spin-coated polymer film. Spin speed and time was 3,000 rpm and 30 sec, respectively. All the samples were handled and processed in a class 100 clean room. Ambient temperature was constant at 22°C, and relative humidity was maintained at 60%. Samples of without spin and with spin were prepared. The adhesive was removed from the refrigerator and allowed to warm up to room temperature before processing. For without spin, small sample quantities were placed on cleaned silicon wafers. For spinning, the films were deposited with a precision spin coater in a glove box. The deposition process involves the dispensing of fluid onto a stationary or slowly spinning substrate. An excessive amount of fluid is used to prevent coating discontinuities caused by the fluid front drying prior to it reaching the wafer edge. Both types of samples were then cured by a typical UV source under the same UV curing profile for different exposure times.

Curing Degree Measurement

For the monitoring of the chemical changes after UV curing, FTIR spectroscopy offers the opportunity of measuring the consumption of the monomer during the curing reaction with high accuracy. In this study, a Perkin-Elmer Spectrum-One FTIR Spectrometer (Norwalk, CT), with a resolution of 16 cm⁻¹ was used. During the curing of the epoxy adhesive, the epoxy resin combines with amine for a chemical cross-linking reaction. The polymerization reaction can be monitored by the C-N stretching vibration band of the amine group at ~1,332 cm⁻¹ (Fig. 1). As polymerization proceeds, the intensity of this band decreases relative to either the initial peak intensity or to an internal reference peak that does not change during polymerization. This yields information about conversion as a function of UV exposure time.

RESULTS

Properties of epoxy adhesive depend on the degree of cross-linking of the curing reaction. In general, the cross-linking of the epoxy resin is the degree of curing, and its completeness determines the rigidity of the cured epoxy adhesive. The chemistry behind the curing of the UV adhesive begins with the formation and linear growth of polymer chains in the epoxy resin that begins to branch and then cross-link. The final structure is a three-dimensional, highly cross-linked chemical network. The curing reaction of epoxy resin proceeds from a rubbery state to a glassy state and becomes hardened.

During epoxy curing, there are hardly any changes in the absorption peculiar to the alkyl groups, carbonyl groups, and benzene rings. The peaks of the epoxy, amino, and hydroxyl groups gradually change. From the results of FTIR analysis, the continual decrease of the tertiary amine band area at 1,332 cm⁻¹ over time shows progressive consumption of the amine group in cross-linking during the curing reaction. Enlarged views of the amine group absorption for different UV exposure time that comprises peaks at 1,332 cm⁻¹ are shown in Fig. 2. The greater the amine band area remained, the less complete the cross-linking and the weaker the chemical bonding, hence, the lower the rigidity of the adhesive. In other words, a lesser amine band area remained at 1,332 cm⁻¹, the more complete the cross-linking, and the stronger the chemical bonding, hence, the greater the rigidity of adhesive.

The curing degree (α) at exposure time, t, can be calculated from the initial area of the amine and a reference peak, A_{amine,0} and A_{ref,0}, respectively, and their corresponding values at time t, A_{amine,t} and A_{ref,t}, according to the following equation: