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Evaluation of the adhesion on the nano-scaled polymeric film systems

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ABSTRACT

We applied scanning acoustic microscopy known as the V(z) curve technique to photoresist thin-film systems for the evaluation of the adhesive strength at the film-substrate interface. Through the measurement of the SAW (Surface Acoustic Wave) velocity, the V(z) curve analysis allows us to quantify the stiffness of the film-substrate interface. In addition, we conducted a nano-scratch test to quantify the ultimate strength of the adhesion through the evaluation of the critical load. To vary the adhesive conditions, we prepared thin-film specimens with three different types of pre-coating surface treatments, i.e., oxygen-plasma bombardment, HMDS (Hexametyldisilazane) treatment and untreated. The magnitudes of the quantified stiffness and ultimate strength are found consistent with each other for all the specimens tested, indicating that the pre-coating surface treatment can strengthen both the stiffness and ultimate strength of the adhesion. The results of this study demonstrate the usefulness of the V(Z) analysis as a nondestructive method to evaluate the adhesion strength of nano-structured thin-film systems.

1. Introduction

In recent years, nano-structured thin-film systems are widely applied in industries (e.g., MEMS/NEMS device, display, optical coating, semiconductor or the like). Thin films are used for many and various purposes such as to provide resistance to abrasion, erosion, corrosion, galling, tarnish, wear, radiation damage, or high temperature oxidation, to reduce friction or electrical resistance, to provide lubrication, to prevent sticking, and to provide special magnetic or dielectric properties. When deposited onto a substrate, the mechanical properties of the film material at the neighborhood of the interface become different from those in a bulk. Therefore, it is important to characterize the mechanical properties of the nano-structured thin film. Many researchers tried to evaluate the properties of thin-film structures such as the film density, grain size, microstructures, elastic properties, and the film/substrate interface condition (e.g. film adhesion strength to the substrate) [1–5]. For the film-substrate system, the film adhesion to the substrate is a critical issue because the existence of degradations or debonds can affect the function of a film system or even causes a complete failure [6]. Over the years, a variety of methods have been applied to measure the adhesion condition, of which the most common are the scotch tape, scratch, peel, and indentation tests. In 1935, Strong suggested the 'scotch tape test', which has been used by numerous works to evaluate the adhesive condition at the thin-film interface [7]. Markus et al. applied a pull-off test to study the adhesion of a photo-definable epoxy coating on the copper surface of a standard PWB substrate [8]. The first detailed work using a scratch method to measure the adhesion was performed by Heavens [9]. In the early 1950s, Heavens used the scratch test method to evaluate the adhesion of chromium films on glass substrates. In this work, a vertical load was applied to the point and gradually increased until a critical value of the load was reached at which the film was completely stripped off the substrate, leaving a clear channel behind. The critical load was determined by examining the resultant scratches made in the film with an optical microscope. The critical load was taken as a measure of the adhesion. Recently, Lauri et al. applied both a scratch test and scotch tape test to evaluate the adhesion of atomic layer deposited thin films on silicon [10].

However, these methods do not maintain the functionality of the films after testing and damage the materials. In other words, these methods are virtually all destructive methods so that evaluation of adhesion necessarily accompanies destruction of the material.

Therefore, it is essential for the evaluation method to be nondestructive so that the functionality of the films is maintained after testing and avoid additional damage.

In this study, we propose the elastic strength (the stiffness) of the interface of thin-film systems as an alternative parameter to evaluate the adhesion strength. Generally, a high elastic modulus

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leads to a high yield stress. Since the effect of work hardening is independent of the elasticity, a high yields stress causes a high ultimate stress. Thus, it is expected that quantification of the elastic modulus of film-substrate interfaces is a way to evaluate the adhesion strength nondestructively.

The aim of this study is to evaluate the elastic modulus of the film-substrate of photoresists prepared under different coating conditions, and compare the results with the ultimate strength quantified by an independent experiment. An acoustic technique known as the Scanning Acoustic Microscopy (SAM) was used to evaluate the stiffness, and a nano-scratcher along with the Laugier theory to assess the critical load of the interface. The results of the study show clear correlation between the observed elastic modulus and critical load, which has led us to a hypothesis that intermittent cleavage of the chemical bonds at the film-substrate interface is the dominant weakening mechanism of the adhesion. This hypothesis is yet to be quantitatively verified by an independent study, but the results of this study have convinced us of the usefulness of the V(z) analysis as a nondestructive method to evaluate thin-film adhesion strength.

2. Theory

2.1. V(z) curve

Fig. 1 shows a schematic diagram of SAW propagation between the acoustic lens and the specimen via a coupling medium (e.g., distilled water). In theory, the oscillations of the received signal can be explained by the interference between the specularly reflected acoustic wave (path #1) and the leaky surface wave (path #2). Leaky surface waves can be generated at a liquid-solid interface if the half aperture angle of the acoustic lens is greater than the second critical angle for the surface. Leaky surface waves can propagate along the specimen surface and radiate energy into the liquid at the critical angle. The leaky surface waves interfere with the specularly reflected acoustic waves at the acoustic sensor. The resultant interference produces alternating maxima and minima in the acoustic output signal as the distance between the acoustic lens and the specimen is varied. The plot of the interference is called the V(z) curve. Here, "V" represents the amplitude of the received signal and is a function of "z", the distance between the specimen and the acoustic lens.

2.2. Calculation of surface acoustic wave velocity

In this study, we used the ray model to calculate the surface acoustic wave (SAW) velocity illustrated in Fig. 1. The ray model is based on the ray interference theory [11]. According to the ray theory, when the specimen is displaced from z = 0 toward the acoustic lens by z (z > 0), the path #1 and #2 respectively experience the following phase change. Here, z = 0 is set when the lens position is such that the focal point is on the specimen surface. As the lens is moved in the negative z direction, the acoustic beam path #2 is increased (Fig. 1). When the specimen is at a distance z from the lens focal plane, the phase lags of $\delta_{\#1}$ (for path #1) and $\delta_{\#2}$ (for path #2) are expressed by:

$$\begin{aligned}\delta_{\#1}(z) &= -2\overline{BO}\cdot k_w = -2\cdot z\cdot k_w \\ \delta_{\#2}(z) &= -\overline{AOC}\cdot k_w + \overline{AC}\cdot k_R\end{aligned} \tag{1}$$

Here $\delta_{\#1}$ and $\delta_{\#2}$ are the phase changes for path #1 and path #2. The relative phase difference between the two paths is given as follows:

$$\begin{aligned}\Delta z &= \delta_{\#2}(z) - \delta_{\#1}(z) \\ &= 2z\cdot\left[k_w\cdot\left(1-\frac{1}{\cos\theta_R}\right)+k_R\cdot\tan\theta_R\right]\end{aligned} \tag{2}$$

where k_w and k_R denote the wavenumber of the acoustic wave in the water between the lens and specimen, and that of the SAW, respectively. A phase change of 2π in the relative phase difference corresponds to the interval between a neighboring pair of dips or peaks in the corresponding V(z) curve, as indicated in Fig. 2. From Eq. (2) and Snell's law, it follows that:

$$\Delta z = \frac{V_w}{2\cdot f\cdot(1-\cos\theta_R)} \tag{3}$$

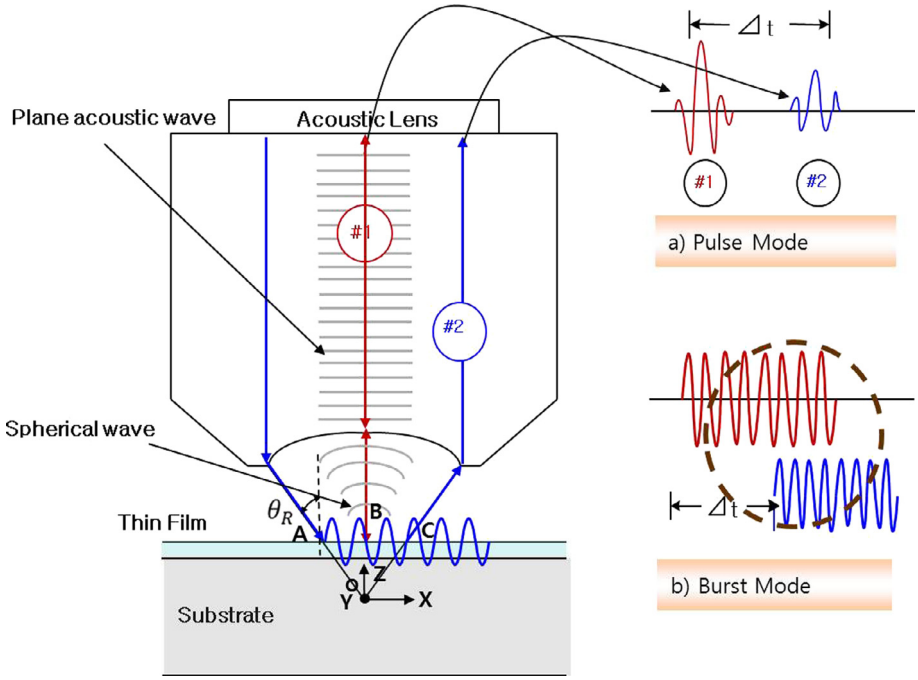

Fig. 1. Schematic diagram showing the principle of the V(z) curve analysis.