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Curing temperature- and concentration-dependent dielectric properties of cross-linked poly-4-vinylphenol (PVP)

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ABSTRACT

In this paper, dielectric properties of various thick PVP films cured at temperatures between 125° C and 200 °C are investigated. The thicknesses of PVP films are adjusted by varying their concentration in PGMEA solvent from 10 wt% to 2.5 wt%. Through FT-IR, *C*–*V*, SEM, and AFM analyses, the optimum curing process temperatures (150 °C for 10 wt% and 7.5 wt% samples, and 175 °C for 5 wt% samples) where PET substrates can be thermally endured are proposed in terms of their low hysteresis voltage in the *C*–*V* curve (1–2 V in 10 wt% samples, below 1 V in 7.5 wt% samples, and 0.5 V in 5 wt% samples).

1. Introduction

Future electronic devices will be required to be flexible, wearable, and transparent for next generation mobile and transparent applications such as electronic-paper, wearable display, flexible touch screen, and transparent wall [1–4]. In light of this, graphene oxide and polymer dielectrics have been proposed for gate and field insulator for flexible and transparent electronics (FTEs) [5,6]. Although graphene oxide and polymer dielectrics have many benefits, such as easy fabrication, low cost, and low process temperature, these still have troubles in achieving excellent dielectric property and film thickness control. Recently, a thick poly-4-vinylphenol (PVP) film has been applied to flexible electronic devices, showing excellent electrical properties [7–9]. However, for future FTEs such as thin film transistors (TFTs) and flash memory devices, it is still important to fabricate thin polymer dielectric layer with (1) high gate capacitance for high drive-in current, (2) increased tunneling probability for low programming/erasing voltage biases, and (3) high transparency corresponding to a certain light wavelength. Until present, it has not been clarified how the thickness of PVP films can be feasibly controlled and also how the thickness affects the electrical property of PVP films. In this letter, we systematically investigate dielectric properties of different thick PVP films obtained by adjusting their concentration. The annealing (or curing) process to induce cross-linking phenomenon in PVP films with poly(melamine-co-formaldehyde) (PMF) is performed at several temperatures, and an optimum process temperature suitable for the fabrication of flexible devices is also proposed in terms of low hysteresis voltage in *C*–*V*.

2. Experiments

PVP powder was mixed with PMF, working as a cross-linking agent, in propylene-glycol-monomethyl-ether-acetate (PGMEA). The mixed solution was then spin-coated at 5000 rpm on (100) p-type Si substrates (1–30 Ω cm) to form an insulating layer. In the first part of experiment, the concentration percentage of PMF to 10 wt% PVP was varied from 0 to 100% (in steps of 50%), and these dielectric films were annealed at 125 °C–200 °C (in steps of 25%) in order to induce the cross-linking process between PVP and PMF. In the second part, we reduced the concentration of PVP from 10 wt% to 2.5 wt% (in step of −2.5 wt%) to achieve thinner PVP films. The annealed samples were then analyzed by Fourier transform infrared (FT-IR) spectroscopy, secondary electron microscope (SEM), and atomic force microscope (AFM). Next, in order to form a metal-insulator–semiconductor (MIS) capacitor, 70 nm thick Ni layer was deposited in a thermal evaporation system through a

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metal shadow mask. Capacitance–voltage (C–V) measurement at 1 MHz was finally performed on the capacitor samples using a semiconductor parameter analyzer (Keithley 4200), extracting hysteresis voltages and dielectric constants for further analysis.

3. Results and discussion

We first investigated the PVP/PMF layers through FT-IR spectroscope to understand their interaction in detail. As shown in Fig. 1(a), hydroxyl (–OH) groups in PVP layer are known to be preferentially bonded with those in PMF through annealing process, which is called a cross-linking process [7]. Fig. 1(b) shows FT-IR spectra of the PVP/PMF layers with different concentration of PMF (0%, 50%, and 100%) annealed at 200 °C, which is known temperature regime to induce a cross-linking process between PVP and PMF [7]. Even though peaks indicating –OH groups were observed around 3000 cm^{-1} ~ 3250 cm^{-1} in the PVP sample without PMF, the peak position slightly moved to higher frequency region around 3250 cm^{-1} ~ 3450 cm^{-1} after adding PMF to PVP. Since –OH groups in PMF are easily cross-linked with those in PVP during the 200 °C anneal [7], PVP and PVP/PMF samples respectively have –OH groups in non-hydrogen and hydrogen bonding states [10]. This difference of bonding states consequently seems to make the –OH-related peaks to shift to different positions.

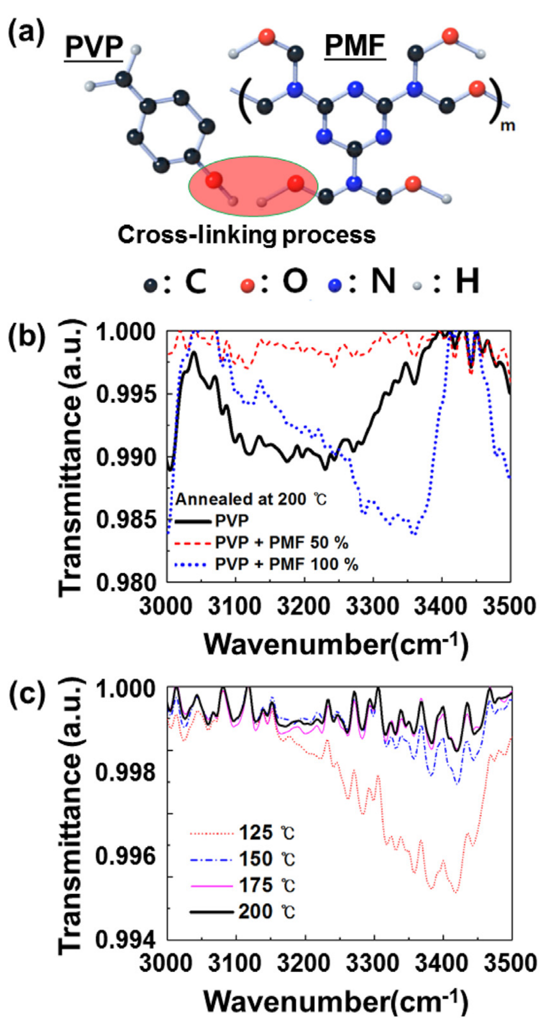

Fig. 1. (a) Schematic diagram for cross-linking process between PVP and PMF. FT-IR spectra of (b) PVP films with various concentration of PMF (0%, 50%, and 100%) annealed at 200 °C and (c) PVP + 50% PMF films annealed at 125 °C–200 °C.

As shown in Fig. 1(b), the PVP sample with 50% PMF shows very low peak intensity, compared to PVP with 0% and 100% PMF samples. It is predicted that the strong peaks in PVP with 0% and 100% PMF samples are respectively attributed to the insufficient cross-linking process between –OH groups in PVP and the remaining –OH groups of PMF after the cross-linking. Through the observations above, 50% PMF was determined to be the proper concentration to yield sufficient cross-link with –OH groups in PVP. However, since the cross-linking process (that removes the –OH groups in PVP) is also dependent on the annealing temperature, FT-IR analysis was performed on the PVP with 50% PMF samples annealed at 125 °C, 150 °C, 175 °C, and 200 °C. As shown in Fig. 1(c), minimum peak intensity was observed in the samples annealed above 175 °C, indicating that sufficient thermal energy above the glass transition temperature (151 °C) of PMF [11] cured the PVP layer. Samples annealed below 150 °C showed relatively high intensity peaks, the lowest peak being observed after 200 °C anneal.

Then, we performed C–V analysis at 1 MHz on Ni-PVP with 50% PMF-Si capacitor samples annealed at 125 °C, 150 °C, 175 °C, and 200 °C in order to investigate the effect of annealing temperature to the dielectric property of PVP films. Fig. 2(a) shows the normalized C–V curve of capacitor sample cured at 200 °C, which is double-swept between –15 V and 10 V. Higher capacitance values were observed when sweeping in the positive direction from –15 V to 10 V. It is thought that the –OH groups remained after the cross-linking process work as hole traps in the interface between PVP and Si. For further analysis, hysteresis voltages and dielectric constants were extracted from the C–V data obtained from the capacitor samples and plotted as a function of annealing temperature in Fig. 2(b). We note that the hysteresis voltage was measured in the region of median capacitance and the dielectric constant was extracted from the accumulation capacitance value. Lower hysteresis voltage (0.7 V) was observed in the 200 °C annealed sample, compared to that (1.8 V) of the 125 °C annealed sample, agreeing with the previous behavior of FT-IR peak values as a function of temperature. The remaining –OH groups confirmed by FT-IR analysis in PVP with/without PMF layers seem to affect negatively

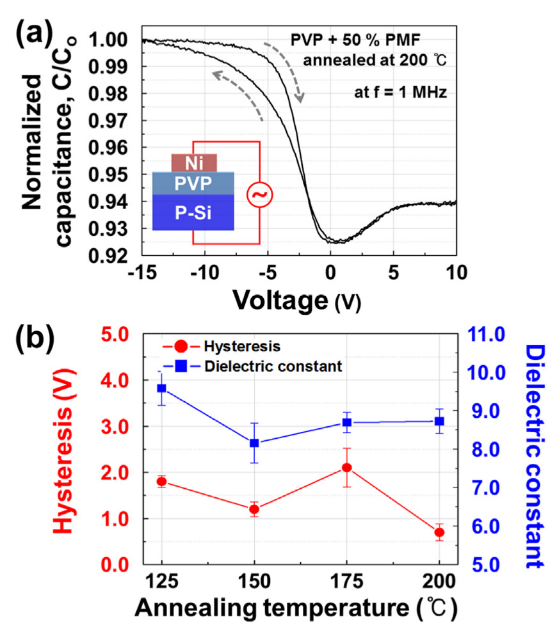

Fig. 2. (a) Capacitance–voltage characteristic of PVP + 50% PMF capacitor sample annealed at 200 °C. The inset shows the cross-sectional schematic diagram of capacitor sample. (b) Hysteresis voltages and dielectric constants of the PVP + 50% PMF films annealed at 125 °C–200 °C.