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Poly(melamine-*co*-formaldehyde) methylated effect on the interface states of metal/polymer/p-Si Schottky barrier diode

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ABSTRACT

The deposition technique and interface effect of polymeric molecules onto silicon surface is crucial topic for organic/inorganic hybrid technologies. In this study, the chemical structure of poly(4-vinyl phenol) (PVP) has been modified by cross-linked agent in solution for deposition onto p-Si surface. The poly (melamine-*co*-formaldehyde) methylated (PMF) has been used as a cross-linked agent for PVP polymeric molecules to apply spin cast deposition technique. The rectification ratio and interface states have been improved with PMF cross-link agent compared with only PVP polymeric layer. Some important diode parameters such as diode ideality factor (η), barrier height (ϕ_b), interface state density (N_{ss}), series resistance (R_s) of the Au/PVP:PMF/p-Si structure were calculated from the current–voltage (*I–V*) characteristics. The ideality factor and barrier height were found to be 2.37 and 0.71. For the explanation of the deviation of ideality factor value from 1, the interface states has been investigated by the frequency dependent capacitance (*C–f–V*) and conductance (*G–f–V*) techniques at room temperature. It is found that the interface states and R_s which indicate the deviation of the ideality factor of Au/PVP:PMF/p-Si structure is strongly depended on bias voltage and frequency.

1. Introduction

Organic materials are one of the most popular topics in the research and development of organic based electronic devices due to their wide range electronic properties which lies from insulator to conductor. For the invention of conductive and semiconductor properties of conjugated organic material structures, there has been big effort on the application electronic devices based on organic materials last two decade [1–3]. The solubility of organic materials provides great advantages on the large area electronic applications that become most promising cost effective materials for use on industrial production due to their low-processing temperature, implementation on different surface and non-vacuum process.

The surface energy of inorganic materials is generally higher than organic materials due to dangling bonds on the surface of inorganic based thin film. Therefore, the organic materials have been used as surface passivation layer between inorganic/metal or organic/inorganic interface for electronic devices in order to match surface energies between two layers. The ultra-thin polymeric insulator has been used as a buffer layer on the metal-oxide surface to enhance charge accumulation and mobility of charge carriers at the dielectric/semiconductor interface for electronic application [4,5]. The main advantage of organic materials is to modify easily the surface energy of organic thin film layer by substituted functional polar or nonpolar group. However, the polymeric insulators usually include some ionic impurities or polar groups that act an interface states to trap charge carriers and also the formation of interfacial layer creates interfacial states [6]. The polar group densities in polymeric molecular structure can be reduced by linking agent between two polymeric chains. A crosslinking agent also improves the formation of polymeric insulator thin film and molecular structure which effect both electrical performance and morphology of device at the semiconductor-insulator interface [7].

The electrical performance of metal–semiconductor device is significantly depended on semiconductor/metal interface that affects charge carrier transports between two layers. For an investigation of interface states, the metal–semiconductor (MS) type Schottky barrier diode (SBD) with organic interfacial layer has been carried out to observe the effect of thin polymer or non-polymer organic layer on the electrical properties, particularly barrier height ϕ_b, ideality factor *n*, interfacial states N_{ss} [8–15]. The poly(4-vinly phenol) (PVP) has been extensively used polymeric structure as an insulator layer on the organic electronics and has

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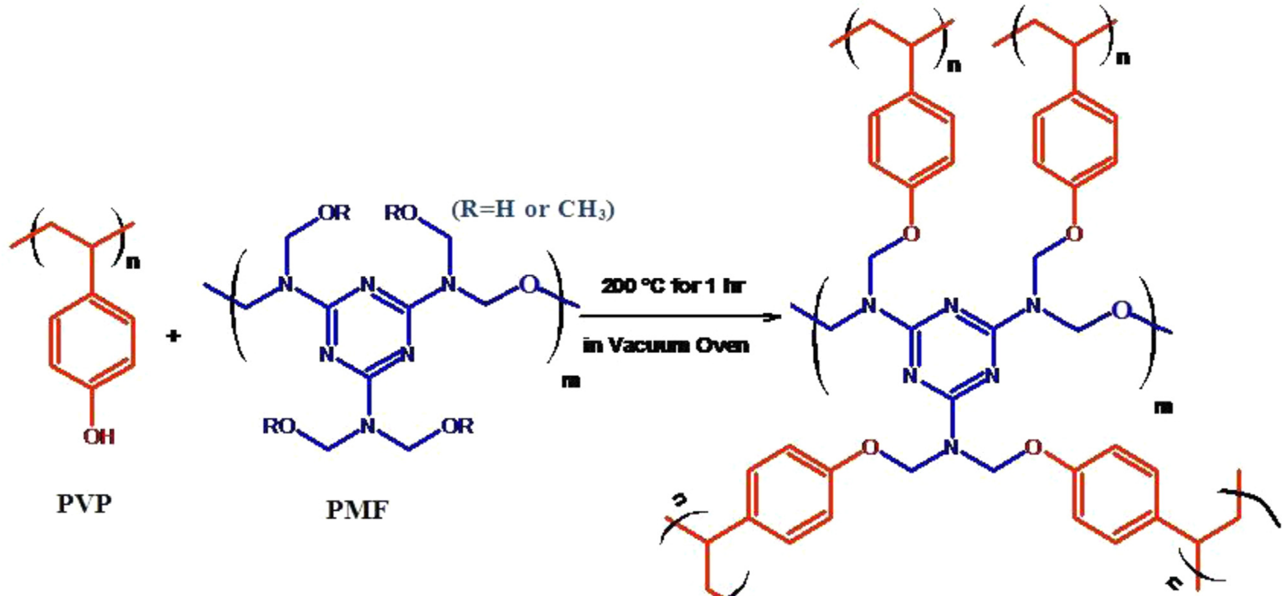

Fig. 1. Chemical structures of PVP, PMF and crosslink reaction mechanism PVP with PMF.

been modified its molecular formation and electrical properties by crosslink agent [7].

Our aim in this study is to investigate the poly(melamine-*co*-formaldehyde) methylated crosslink agent effect on the electrical characteristics of Au/PVP:PMF/p-Si SBD structure by the use of frequency dependent capacitance/conductance measurements and to compare with the electrical parameters of SBD device with only PVP interfacial layer reported our previous study [16].

2. Experimental

Au/PVP:PMF/p-Si SBD structures were fabricated on the 3-inch diameter float zone <111> p-type (boron-doped) single crystal silicon wafer with a thickness of 600 μm and a resistivity of 5–10 Ω.cm. The Si wafer was cleaned through RCA cleaning procedure consisting of organic clean, oxide strip and ionic clean steps [17]. All clean process are performed as removal of insoluble organic contaminants with a 10-minute boiling in $NH_4OH + H_2O_2 + 6H_2O$ solution, removal of a thin silicon dioxide layer using a diluted $HF:H_2O$ (1:10) solution for 30 s. and followed by a 10-minute boiling in $HCl + H_2O_2 + 6H_2O$ solution, respectively. The Si wafer was dried in N_2 atmosphere at the end of each step and immediately transferred to glove box after all cleaning process were completed. Before the deposition of thin film polymer layer on the Si wafer, the high-purity aluminum (99.999%) with a thickness of 1200 Å was thermally evaporated from the tungsten filament onto the whole back surface of the Si wafer under the pressure of 2×10^{-6} Torr. In order to obtain a low-resistivity ohmic back contact, Si wafer was sintered at 570 °C for 5 min in N_2 atmosphere at high temperature tube oven.

The PVP:PMF blend was prepared from 2.5% (w/v) solution in propylene glycol methyl ether acetate (PGMEA, Sigma Aldrich) with weight ratio 1:1 and stirred overnight. The PVP (Sigma–Aldrich) with molecular weight 20.000 and the PMF (Sigma–Aldrich) were used without further purification. To compare of current–voltage characteristics of the Au/PVP:PMF/p-Si structure with Au/PVP/p-Si, the PVP was dissolved in PGMEA at the same weight ratio to obtain 2.5% (w/v). The spin coating technique was applied to deposit PVP:PMF and PVP layers on the front surface of the Si wafer at 4000 rpm for 45 s. The PVP:PMF was thermally cured at 200 °C for one hour in vacuum oven to enforce cross-linking of PVP:PMF polymer and cooled down over night. The thickness of film layer was measured as 250 Å from AEP Nanomap-500LS profilometer. The molecular structures of PVP, PMF and the crosslink reaction PVP with PMF cross-linker are given by Fig. 1.

Au rectifying metal electrode (purity 99.99%) with a thickness 100 nm was deposited on the front surface of p-Si coated with PVP:PMF in a high vacuum under the pressure of 1×10^{-6} Torr using shadow mask. The thickness of metal layer was measured by using Inficon SQM 160 thickness measurement system.

The current–voltage (*I*–*V*) characteristics of fabricated MPS device were measured using a Keithley 2400 programmable current–voltage source meter. The forward and reverse bias capacitance–voltage (*C*–*V*) measurements were performed by using a Keithley 4200 semiconductor characterization system and with a test signal of 20 mV_{rms} . All measurements were carried out at room temperature and in a dark environment. The Au/PVP:PMF/p-Si structure is given in Fig. 2.

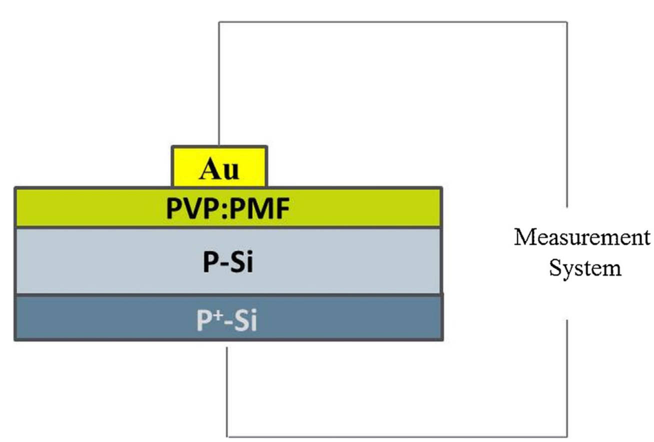

Fig. 2. Cross sectional diagram of PVP:PMF/p-Si structure.