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Amorphous silicon carbide thin films (a-SiC:H) deposited by plasma-enhanced chemical vapor deposition as protective coatings for harsh environment applications

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ABSTRACT

We investigated amorphous silicon carbide (a-SiC:H) thin films deposited by plasma-enhanced chemical vapor deposition (PECVD) as protective coatings for harsh environment applications. The influence of the deposition parameters on the film properties was studied. Stoichiometric films with a low tensile stress after annealing (<50 MPa) were obtained with optimized parameters. The stability of a protective coating consisting of a PECVD amorphous silicon oxide layer (a-SiO_x) and of an a-SiC:H layer was investigated through various aging experiments including annealing at high temperatures, autoclave testing and temperature cycling in air/water vapor environment. A platinum-based high-temperature metallization scheme deposited on oxidized Si substrates was used as a test vehicle. The a-SiO_x/a-SiC:H stack showed the best performance when compared to standard passivation materials as amorphous silicon oxide or silicon nitride coatings.

1. Introduction

The use of wide band gap semiconductors enables the operation of sensor devices and electronics in harsh environments [1]. Target applications range from exhaust gas to pressure sensing for automotive, power plant and aerospace applications [2].

Despite the excellent properties of wide band gap substrate materials, the lifetime of devices is still limited by the stability of the metallizations and the Ohmic contacts. Due to its high melting point ($T_m = 1772$ °C) and its resistance to oxidation, Pt is the standard material for high temperature metallizations. However, Pt metallizations suffer from morphological and electrical degradation when operated at 500 °C and above [3,4]. Furthermore, the Ohmic contacts to wide band gap semiconductors are also affected by degradation when exposed to high temperature and oxygen-rich environments, due to oxygen diffusion into the contact [5,6]. A stable passivation is thus needed to meet the stability requirements.

Due to their excellent mechanical and chemical stability and their back-end compatible deposition temperature ($T_d < 400$ °C) [7–9] amorphous silicon carbide thin films (a-SiC:H) deposited by plasma enhanced chemical vapor deposition (PECVD) are promising protective coating candidates for applications in harsh environments.

In this paper, the influence of various deposition parameters on the a-SiC:H film properties was studied. The performance of optimized layers was then compared to that of standard passivation materials as PECVD amorphous silicon oxide (a-SiO_x) and amorphous silicon nitride (a-SiN_y). For the material characterization presented in this paper, a Pt-based high-temperature metallization scheme deposited on oxidized Si substrates was used as a test vehicle. We expect our results to be applicable to a wide range of harsh environment sensor configurations.

2. Experimental details

Amorphous silicon carbide films (a-SiC:H) were deposited on oxidized Si substrates by means of an Oxford Instruments PL100 PECVD reactor, using SiH_4 (100%) and CH_4 (100%) as precursor gasses and Ar as carrier gas. The Ar flux was 180 sccm and the total flux was mantained constant at 200 sccm. The gasses entered the reaction chamber through a conventional showerhead electrode. A RF generator with a frequency of 150 kHz was employed. Typical deposition parameters were 200 W, 133 Pa (1 Torr) and 400 °C. The film thickness was typically 250 nm.

The chemical composition of the a-SiC:H films was studied by means of X-ray Photoelectron Spectroscopy (XPS) using a Physical Electronics PHI Quantera SXM system. The XPS spectra were obtained using a monochromatic Al K_α source. The measurements were done after a 120 s presputtering with Ar^+ ions to remove surface contaminations. The nominal sputter rate was about 7 nm/min for

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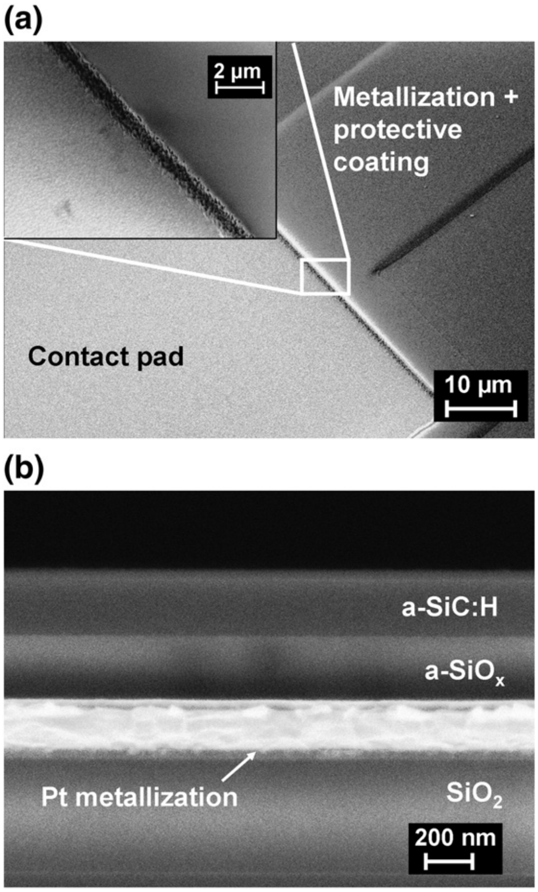

Fig. 1. Tilted SEM micrograph on an a-SiO$_x$/a-SiC:H stack patterned to open the contact pads of the Pt metallization (a) and SEM cross-sectional micrograph of an a-SiO$_x$/a-SiC:H sample in the as-processed state (b).

SiO$_2$. The system was calibrated through a measurement on a bulk Si reference. The charging shift of the peaks was corrected through the O 1 s signal of the samples, since this signal was originated by a background in the system and was independent of the deposition parameters. The position of the peaks was determined through Gaussian–Lorentzian fitting with the software provided by the manufacturer. Wafer bow measurements were carried out with a Tencor FLX-2320 system. The film stress was monitored in the as-deposited state and after a 5 h furnace anneal at 600 °C in synthetic air.

The film thickness and the optical properties of the films were determined by means of spectroscopic ellipsometry (SE). A Sentech Instruments SE800 ellipsometer was employed for these measurements. The measurements were carried out in the VIS + IR range. The fitting to the experimental data was carried out with the software supplied by the manufacturer. The film thickness was also confirmed by scanning electron microscopy (SEM) cross section measurements. The specific resistivity was measured on films deposited on oxidized substrates by means of four-point resistance measurement at room temperature and at 600 °C.

Table 1
Composition, Si 2p and C 1 s peak positions, deposition rate and refractive index at 630 nm as a function of the SiH$_4$/CH$_4$ ratio for films deposited at 400 °C, 200 W and 133 Pa.

Sample	SiH4/CH4	Si (at%)	C (at%)	O (at%)	Si 2p (eV)	C 1s (eV)	Dep. rate (nm/min)	n (630 nm)
1	0.60	68.5	29	2.6	99.78	283.26	25.0	3.11
2	0.33	56	41.1	2.6	99.97	283.32	21.8	3.11
3	0.25	50.2	47	2.6	100.28	283.65	24.4	2.80
4	0.18	39.5	57.9	2.7	100.37	283.84	22.8	2.69
5	0.14	36.9	61.4	1.7	100.29	283.81	24.7	2.52

Table 2
Layout of the samples fabricated for the environmental testing.

Sample name	Metallization	Thickness [nm]	Protective coating	Thickness [nm]
a-SiO$_x$/a-SiC:H	Ti/TiN/Pt/TiN/Ti	20/10/150/10/20	a-SiO$_x$/a-SiC:H	250/250
a-SiO$_x$	Ti/TiN/Pt/Ti	20/10/150/20	a-SiO$_x$	500
a-SiN$_y$	Ti/TiN/Pt/Ti	20/10/150/20	a-SiN$_y$	500

Finally, the optimized a-SiC:H films were deposited on Pt-based metallization patterns for a comparison with standard passivation materials. Polished 100 mm Si substrates (p-type, CZ) were initially coated with a 500 nm LPCVD SiO$_2$ layer using tetra-ethyl-ortho-silicate (TEOS) as precursor. A two-layer lithographic process with a lift-off resist (LOR) was performed, followed by the deposition of the metallization stacks and lift-off. The metallizations consisted of a sputtered Ti/TiN/Pt/TiN/Ti stack with nominal thicknesses of 20/10/150/10/20 nm, whereas all layers were sputtered subsequently without breaking the vacuum. A 250 nm PECVD a-SiO$_x$ layer was deposited on the metallizations using a TEOS precursor, followed by the 250 nm a-SiC:H layer. The a-SiO$_x$ layer is necessary since a-SiC:H films provide insufficient electrical insulation at high temperatures (see Section 3.1). The a-SiO$_x$/a-SiC:H stack was patterned to expose the contact pads. A sputtered AlN layer was used as hard mask. The AlN layer was deposited through DC reactive sputtering in N$_2$/Ar atmosphere and patterned through wet etching in phosphoric acid at 80 °C. A two-step ICP-based etch process was employed to etch the a-SiO$_x$/a-SiC:H passivation stack. In the first step, the a-SiC:H layer was etched in SF$_6$/O$_2$ chemistry. An etch rate of 180 nm/min for the a-SiC:H layer and a selectivity of 30:1 toward the AlN hard mask were achieved with this process. In the second step, the a-SiO$_x$ layer was etched in a CF$_4$ process. In this etch process also the thin Ti/TiN films on the Pt metallization were removed and the etching stopped thus on the Pt layer, as was demonstrated by EDX measurements. The AlN hard mask was then finally removed in phosphoric acid (80 °C). A tilted SEM micrograph and a SEM cross-section of the Pt metallization patterns passivated by an a-SiO$_x$/a-SiC:H stack are shown in Fig. 1. For a comparison, similar samples with standard passivation materials were also fabricated. The layout of the processed samples is summarized in Table 2. The adhesion of the passivation stack on the metallizations was investigated through scratch tests. This analytical tool allows a quantitative measurement of the adhesion strength of thin films and the identification of material-specific failure modes [10]. A CSM nano scratch

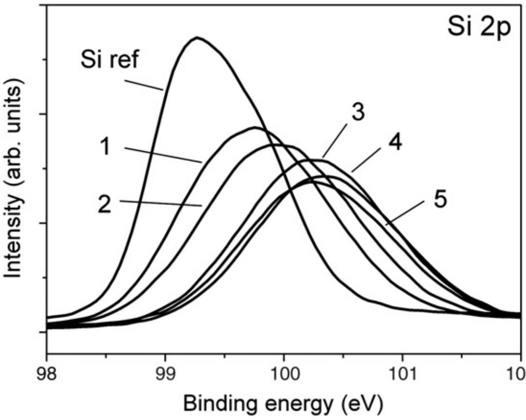

Fig. 2. XPS narrow scans of the Si 2p peak for films deposited at 400 °C, 200 W and 133 Pa with varying SiH$_4$/CH$_4$ gas ratio (see Table 1).