Influence of the annealing condition on the BN bonds intensity detected by FTIR characterization

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Abstract

In this work, we present infrared spectroscopy characterizations of poly-Si/NIDOS bi-layer films used as gate structure in standard complementary metal-oxidesemiconductor (CMOS) technology. These layers are obtained by low pressure vapour deposition (LPCVD) technique. The film consists on an amorphous silicon in-situ doped nitrogen (NIDOS) layer onto which is deposited a polysilicon in-situ doped boron (PolySi) layer. These PolySi/NIDOS bi-layer structures are deposited on oxidized monocrystalline silicon, and annealed at 600 C and 700 C for different durations. Finally, the variations of the films chemical constitution are studied by Fourier transform infrared spectroscopy (FTIR). This analysis clearly shows the preservation the oxide quality by the formation of the BN bonds in the NIDOS/SiO₂ interface.

1. Introduction

The bi-layer thin films play an important role in various fields of modern science and technology. Novel devices are being extensively fabricated using thin film technology and the role of the structure and composition at the surface and interface of the materials governs the performance of such devices in particular Metal-Oxide-Semiconductor (MOS) transistors [1-3]. The main aim of the different works in this domain is to avoid the boron diffusion into silicon substrate through the gate oxide films [4-7]. This crucial problem induces several degradations of the gate-oxide characteristics which make necessary to maintain the quality of the interface gate/oxide. Our contribution in this domain is to propose a study infrared spectroscopy characterization of new polySi/NIDOS/SiO₂ structure for CMOS technology.

2. Materials & methods

The samples consist of two polysilicon layers deposited by LPCVD, on oxidized single crystal silicon substrates. Thin NIDOS layer (about 0.2-µm-thick) is in-situ nitrogen doped silicon obtained from mixture of disilane Si₂H₆ and ammonia NH₃ gases. On this later, a second polysilicon layer deposited by the disilane and boron trichloride (BCl₃) was also in-situ boron doped (about 0.13-µm-thick). All samples have been thermally annealed in a classic vertical furnace at 600°C and 700°C for different durations. Finally, the samples were performed by FTIR analysis to the aid of a device type 360 Avatar. This technique allows determining the different chemical bonds it also shows the evolution of the peaks depending on the annealing conditions.

3. Results and discussion

3.1. Films annealed at 600 C

Figure 1 show The IR absorption spectra recorded between 400 and 4000 cm⁻¹ of the polySi / NIDOS films annealed at 600°C for different durations.

All the spectra show, that the signification absorption peaks are located between 600 and 1500 cm⁻¹ "Fig.2".



Fig. 1. Variation of the FTIR spectra polySi/NIDOS/oxide structure with annealing duration at 600°C

The peak situated around 1400, 1080, 1040 and 912 cm^{-1} , which can be associated to BN bonds [8-12] and the peaks positioned at 735, 750, 782 and 815 cm⁻¹, which is assigned to the B-N-B bond [13-15]. Moreover, the absorption bonds located at 860, 1320 and 1250 cm⁻¹ assigned to the Si-N bond [16-18].

Figure 2 show that the absorption intensity of the peaks B-N-B and Si-N decrease when the annealing duration increases. This can be explained by the dissociation of these bonds, which can improve the films conductivity by boron atom detachment in silicon matrix. Moreover, we find a variation of strong absorption bond situated from 1000 to 1500cm-1 according increasing times, which requires a deconvolution (Fig.3).



Fig. 2. The principal peaks appear in the wave number located between 600cm⁻¹ and 1500cm⁻¹ for PolySi/NIDOS films.

The deconvolution of theses curves are reported in figures 3 (a, b and c), we observe the emergence of Si-N and BN peaks located at different wave numbers. In addition, the deconvolution allowed us to detect the crystalline form of BN bond, hexagonal boron nitride (h-BN) and cubic boron nitride (c-BN). The table 1 recapitulated Wave numbers of IR absorption bonds collected from various publications.

 Table1. Wave numbers of IR absorption bonds collected from various publications

Wave number (cm ⁻¹)	Absorption corresponding bond	References
1150, 1150, 1250	Si-N	[16,18]
1370, 1350, 1380	h-BN	[13,14]
1070, 1081, 1085, 1097, 1116	c-BN	[9,10,11]





Fig. 3. Deconvolution of the absorption band located between 1000 cm^{-1} and 1500 cm^{-1} .

From the deconvolution results, we have plotted the variation of Si-N, h-BN and c-BN peaks situated at 1250, 1400, 1450 and 1092 cm⁻¹ respectively versus annealing duration (Fig.4).

Figure 4, show a slight decreasing of the all absorption intensity bonds for periods less than 120 minutes, this can be explained by partial dissociation of the complex.



Fig. 4. Evolution of the intensity of Si-N, h-BN and c-BN peaks versus annealing duration

Moreover, beyond 120 minutes, we observe the increasing of the absorption intensity of the c-BN and h-BN peaks. This can be interpreted by the decreasing of the Si-N and B-N-B bond, where the dissociation of these later peaks (Si-N and B-N-B) during the duration increasing encourages the formation of the h-BN and c-BN complex. In addition, we see that the absorption intensity of the c-BN peak is two times greater than the h-BN, this result is in concordance by the works of the two author's W.Takayuki et al and W.Chengbiao [19-21].

3.2. Films annealed at 700 C

The results obtained by FTIR allow the detecting of chemical bonds in the films polySi/NIDOS annealed at 700°C for different durations. The results showed the appearance of several bonds in the material "figure 5".



Fig. 5. Variation of the FTIR spectra polySi/NIDOS/oxide structure with annealing duration at 700°C.





We are interested the bonds related to nitrogen atom, which located from 600cm⁻¹ to 1500 cm⁻¹ "Fig. 6". This zone revealed

the formation of various peaks as, The B-N-B bond located around 735 cm^{-1} and 750 cm^{-1} [13-15].

In addition, the peaks situated approximately at 626 cm⁻¹, 1092 cm⁻¹ and 1400 cm⁻¹ which is assigned to the B-N bond. Moreover, the Si-N peak is located at 860, 890 cm⁻¹, 900 cm⁻¹, 1150 cm⁻¹ and 1250 cm⁻¹. Furthermore, we find two large absorption bonds located between 1000-1300 cm⁻¹ and 1350-1450 cm⁻¹ respectively, which require deconvolution "Fig.7".



Fig. 7. Deconvolution of the absorption band located between 1000 cm^{-1} and 1500 cm^{-1} .

The deconvolution results show the appearance of the Si-N located 1150 and 1200 cm⁻¹, and the emergence of two peaks assigned to the h-BN and c-BN located respectively at 1400, 1540, and at 1090cm⁻¹. For the follow the evolution of these peaks, we have plot the variation of absorption intensity depending on the duration of annealing (see figure 8). The fig. 8 shows the increasing of the Si-N bonds and the decreasing of the c-BN and h-BN bonds for periods less 120 minutes. Beyond 120 minute we find that this phenomenon is reversed (the decreasing of Si-N and increasing of c-BN and h-BN bonds), this can be explained by the dissociation of the Si-N and B-N-B bonds in the matrix witch encourage the h-BN and c-BN formation as complex.



Fig. 8. Evolution of the intensity of Si-N, h-BN and c-BN peaks versus annealing duration.

In addition, we notice that the absorption intensity of the c-BN complex is two to three times greater than the h-BN complex. About this remark, we can say that the concentration of the c-BN complex in the matrix is more imported than the h-BN bonds. This result is in good agreement with the results of the Takayuki et al [20] on the study of the effect of bias application on c-BN synthesis by induction thermal plasmas under atmospheric pressure. The injection of the BCl₃ is known to be very efficient for extreme hardness c-BN synthesis. In plus, the obtained results are in good concordance with Chao et al [20] on polycrystalline films implanted boron and nitrogen. Increasing the amount of nitrogen in the films increased the density of BN pairs who oppose the diffusion of boron atoms in preventing them from reaching the substitutional sites.

4. Conclusion

The Infrared spectroscopy characterization of bi-layer films deposited by LPCVD has been studied. The FTIR analysis was carried out after the heat treatment. The physico-chemical characterizations indicated the remarkable presence of the h-BN and c-BN complex, and the absorption intensity of the c-BN is always greater than the h-BN during duration increasing. Moreover, the thermal stability of the c-BN complex is maintained by the quasi constancy of the absorption intensity versus the temperature variation. In addition, the presence of complex as hard as the c-BN interface in polySi/NIDOS provides an effective preservation of the oxide layer. These results suggested the use this material as gate structure for microtechnology applications.

5. References

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