

Stability of boron and phosphorus implanted tungsten silicide structures at high temperatures

R. Bashir^{a)} and F. Hebert^{b)}

School of Electrical and Computer Engineering, Purdue University, West Lafayette, Indiana 47906

(Received 8 October 1999; accepted 28 April 2000)

We report on the stability of sputter-deposited tungsten silicide ($\text{WSi}_{2.6}$) films that were implanted with boron or phosphorus and annealed at high temperatures using rapid thermal annealing. Depending on process conditions, some films were found to be unstable, resulting in peeling and lifting from the substrate. The regime of stability was experimentally determined and found to be a function of the implant dose, species, and anneal temperature. Films implanted with boron were found to be more stable than those implanted with phosphorus. With the appropriate choice of dopant dose, anneal temperature, and capping layer type, the film stacks were found to be stable upon subsequent furnace annealing steps at 900 °C. © 2000 American Vacuum Society. [S0734-211X(00)04304-3]

I. INTRODUCTION

Since the earlier reports of the use of tungsten silicide for integrated circuit applications,^{1,2} there have been numerous reports of the use of this material for bipolar extrinsic base regions,³ metal-oxide-semiconductor gate structures,⁴ EEPROMs,⁵ and related applications.⁶ Stacks of polycrystalline silicon and silicide (polycides) have the benefit of having a lower resistivity than heavily doped polysilicon. Most popular polycide and silicide structures, however, are not stable at high temperatures. For example, TiSi_2 forms a high resistance contact to P+ silicon due to the formation of Ti-B compounds at temperatures above 950 °C. Furthermore, TiSi_2 and CoSi_2 agglomerate when exposed to temperatures in excess of 1000 °C, resulting in increased sheet resistance. This is inconsistent with the use of such materials for integrated circuit manufacturing.

Tungsten silicide films can be stable up to temperatures in excess of 1100 °C. These films can be formed using chemical vapor deposition (CVD) or rf sputtering. The stability of CVD tungsten silicide films upon furnace oxidation can be improved upon reduction of internal stresses by a rapid thermal processing and by increasing the Si/W ratio to greater than 2.6.⁷ Stacking the films in layers of polycrystalline silicon has also shown to improve their stability.⁸ These films can also be implanted specifically to be used as a dopant diffusion source, or become implanted inadvertently when being used as a mask. There are no reports in the literature on the stability of tungsten silicide films after ion implantation and rapid thermal annealing.

The purpose of this article is to report, for the first time, on the preliminary experimental results of stability of tungsten silicide films that were implanted and subsequently rapid thermal annealed. A stability regime was experimentally determined and it was found that boron doped films were more stable than phosphorus doped films.

II. EXPERIMENTS AND RESULTS

The experiments were performed on 5 in. wafers without any patterns. After the deposition of a thin layer of polycrystalline silicon of 1500 Å in thickness on the silicon surface, the tungsten silicide layer was deposited in a sputtering system (Varian model 3280) using a target of composition $\text{WSi}_{2.8}$. The resulting film had a composition of about $\text{WSi}_{2.6}$. The resistivity was extracted from a series of depositions of increasing time and thickness of the film and was found to be about $7.8 \times 10^{-4} \Omega \text{ cm}$. This is consistent with earlier reports of such films. The film thickness used in the experiments here was about 1000 Å. The wafers were then implanted with a series of doses ranging from a dose of 6×10^{14} to $3 \times 10^{16} \#/\text{cm}^2$. The energy of all implants was kept at 20 keV. A capping insulator layer was then deposited over the surface of the film consisting of a 2000 Å undoped oxide layer deposited using thermal decomposition from a tetramethylorthosilicate (TEOS) source. The wafers were then annealed in an AG4108 rapid thermal processor for 30 s each at 1050, 1100, and 1150 °C in an N_2 ambient. The wafers were inspected after anneal and the film was defined to be unstable if the defect density exceeded $1/\text{cm}^2$. The defects were defined to be any regions where the film had peeled, lifted off, or cracked, as observed visually under a 500× magnification. Figure 1 shows an optical micrograph of the regions showing the regions where the films had cracked and peeled in circular shapes.

The dose of the implant species was found to have a significant effect on the stability. This behavior is shown in Figs. 2 and 3, which are plots showing final annealing temperature versus dopant dose for boron and phosphorus implanted silicide/polycide films. These figures show the regions of stability and instability for the doped films. The graph clearly shows the combinations of anneal temperature and dopant dose which form regions of implanted film stability and instability (peeling). As can be seen from Fig. 2, boron may be used at doses up to approximately $1 \times 10^{16} \#/\text{cm}^2$ to obtain films which are stable at temperatures up to 1100 °C. As shown in Fig. 3, phosphorus can be used at

^{a)}Author to whom correspondence should be addressed; electronic mail: bashir@ecn.purdue.edu

^{b)}Now with Linear Technology Corporation, Milpitas, CA.

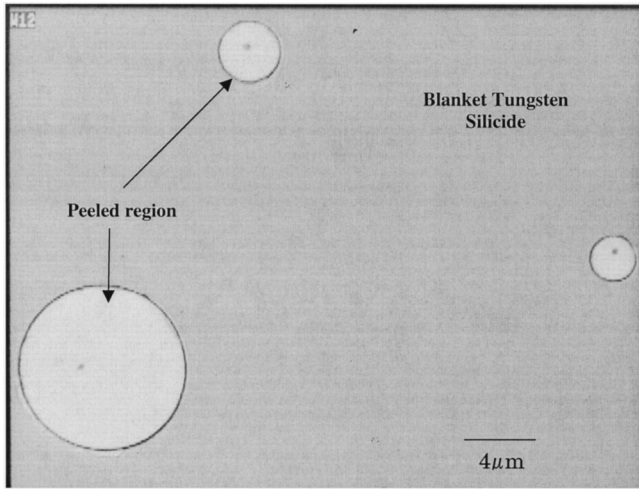


FIG. 1. Optical micrograph (500×) of the region of tungsten silicide peeling.

doses up to approximately $4 \times 10^{15} \text{ #/cm}^2$ to obtain films which are stable at temperatures up to 1050 °C. The difference in the behavior of phosphorus and boron can be attributed to changes in film stress upon the introduction of these species of different sizes. Boron is a smaller atom than phosphorus and is expected to produce less perturbation and stress in the amorphous structure of the tungsten silicide. Upon substitutional incorporation of boron or phosphorus in single crystal silicon, the damage from boron is typically harder to anneal since the difference in atomic size between boron and silicon is larger than that of the difference between phosphorus and silicon. In amorphous tungsten silicide however, the situation can be different and the real reason for increased stability with boron implantation when compared to phosphorus is not totally clear and needs more investigation. It can however be postulated that the incorporation of phosphorus increases the stress in the films making them more unstable and susceptible to peeling. It should also be

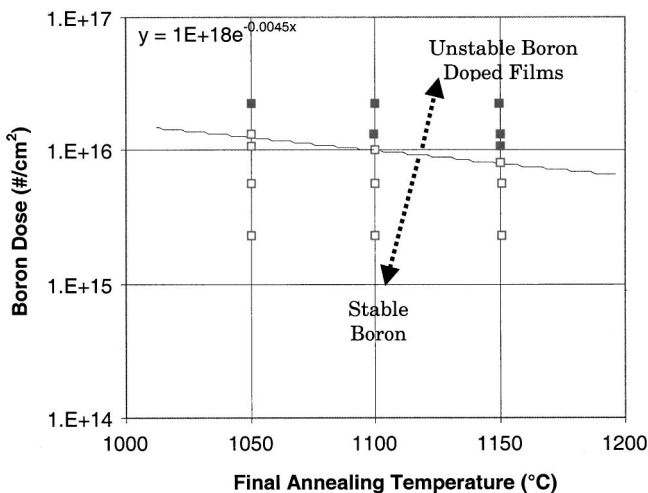


FIG. 2. Boron dose vs final annealing temperature. The region below the dashed line is for stable boron doped $\text{WSi}_{2.6}$ films.

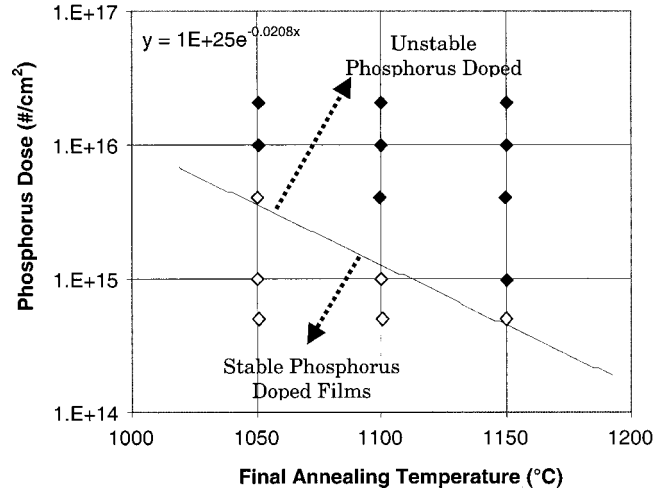


FIG. 3. Phosphorus dose vs final annealing temperature. The region below the dashed line is for stable phosphorus doped $\text{WSi}_{2.6}$ films.

pointed out that in the given experiments, undoped tungsten silicide films were stable even when exposed up to 1200 °C for 30 s.

It was also found that the composition and thickness of the insulator layer deposited on the silicide/polycide layer had an effect on the stability of the film. When a 2000 Å thick oxide film is deposited from a TEOS source thermal decomposition is used as the insulator on top of the silicide layer, and the stack is stable up to a rapid thermal anneal (RTA) temperature of 1100 °C. When a densification anneal step at 900 °C for 20 min in dry oxygen was used after the deposition of the oxide, the stack/films were not stable at 1100 °C. When the densification step was performed in nitrogen, the stack was stable at 1100° RTA step. The nitride/oxide stack on silicide could be the preferred insulator configuration for the silicide/polycide capping layer since this could possibly permit the use of thinner oxide layers with oxidizing ambients (because the nitride blocks the oxygen diffusion).

III. CONCLUSIONS

In this work, we experimentally determined the regions of stability for sputter deposited tungsten silicide films after implantation and RTA. Boron implanted films were found to be more stable when compared to phosphorus implanted films, possibly due to increased stress in the silicide film after implantation. Experimentally obtained data showing the stability region versus implant dose has also been presented.

ACKNOWLEDGMENT

The work was done at National Semiconductor Corporation, Sunnyvale, CA.

¹F. Mohammadi and K. C. Saraswat, J. Electrochem. Soc. **127**, 450 (1980).
²K. C. Saraswat, D. L. Brors, J. A. Fair, K. A. Monnig, and R. Beyers, IEEE Trans. Electron Devices **30**, 1497 (1983).

³K. C. Brown *et al.*, Proc. SPIE **2875**, 48 (1996).

⁴H. Kuo-Ching, F. Yean-Kuen, Y. Dun-Nian, C. Chii-Wen, L. Mong-Song, H. Jang-Cheng, S. Chi-Wen, and K-Y. Lee, IEEE Electron Device Lett. **20**, 36 (1999).

⁵K. Ogier-Monnier, P. Boivin, and O. Bonnaud, Proc. SPIE **3507**, 175 (1998).

⁶S. Wolf, *Silicon Processing for the VLSI Era*, Process Integration, Vol. 2 (Lattice, 1990), pp. 162–169.

⁷A. P. Blosse, Rapid Thermal and Integrated Processing VII, Symposium of the Materials Research Society, 1998, p. 371.

⁸K.-Y. Lee, Y.-K. Fang, C.-W. Chen, M.-S. Liang, and J.-C. Hsieh, IEEE Electron Device Lett. **18**, 181 (1997).