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CONTROL OF A SELF-ALIGNED W SILICIDE PROCESS BY ANNEALING AMBIENCE

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Résumé: Pour les technologies submicroniques, des étapes de métallisation autoalignées sont de plus en plus nécessaires. La formation autoalignée du siliciure de tungstène WSi_2 par réaction entre W et Si a pu être maîtrisée en réalisant des recuits sous oxygène et sous ammoniac. La formation latérale du siliciure est alors évitée même sur des espaciers d'oxyde d'épaisseur 60 nm.

Abstract: With devices at submicronic dimensions, self-aligned processes are becoming of increasing interest. The self aligned W silicide formation by localised reaction between W and Si has been controlled using reactive atmosphere, oxygen and ammonia, during furnace annealing. No lateral silicide formation over SiO_2 spacers, only 60 nm thick, has been observed.

1-INTRODUCTION

Refractory metal silicides are more and more widely used in semiconductor technology due to their resistivity as materials for gate interconnections, contacts on source and drain areas, and as a first buried metallic layer for local interconnections. For ultra large scale integration, with devices at submicronic dimensions, self aligned silicidation is becoming of increasing interest. The self aligned process can be achieved either by selective deposition of the silicide layers or by direct reaction, induced by thermal annealing, between the refractory metal deposited over the whole wafer and the underlying silicon occurring only at localised points where these two materials come into contact. On the other hand the reaction between the refractory metal and oxidized silicon surface cannot take place. This latter approach is known as the salicide process. The critical step in such a scenario consists of the ability to well control the metal silicon reaction to avoid any lateral silicide formation over SiO_2 spacers, only a few thousand angstroms wide separating the silicide areas. Without this control bridging between the gates sources and drains could occur.

To make sure that the silicide process works properly the operating range for annealing time and temperature must be large enough to allow for control and reproducibility of the process. For this it appears necessary to slow down the silicide growth kinetics by inducing, at the surface of the metal layer, a second reaction between the metal and a reactive annealing atmosphere. Consequently a stable state of equilibrium will be reached between the metal silicide phase and the metal compound formed with the reactive atmosphere. Titanium is the refractory metal by far the most widely accepted for this technology [1]. The $TiSi_2$ growth kinetics has been found to be blocked by the formation of $TiNi_x$ compounds during thermal annealing under an N_2 flow. This paper presents recent decisive progress towards the control of the self aligned W silicide formation.

2-EXPERIMENTAL

Up to now silicide technology has not worked using W. It is difficult to achieve on the W/Si reaction due to the high sensitivity of the reaction to small amounts of oxygen both at the W/Si interface and trapped in the W layer during metal deposition [2]. Moreover tungsten does not react with N_2 . On the contrary W reacts with oxygen, but in this case the reaction occurs so fast that tungsten is completely oxidized before the silicide reaction even begins. Recently W nitridation has been studied using ammonia. The WN_x compounds growth kinetics start at 550°C but seem to occur too fast compared with the W silicide formation which is generally blocked.

To overcome these difficulties encountered when using oxygen or NH_3 as the reactive annealing atmosphere the following solution has been envisaged. The WO_x and WN_x growth kinetics can be controlled by limiting the amount of reactive gas (oxygen or ammonia) in the annealing atmosphere. Consequently these reactions can be slowed down enough to allow W silicide formation at the W/Si interface. By varying the oxygen (or NH_3) partial pressure in the annealing atmosphere it is perfectly possible to control the state of equilibrium between the WO_x (or WN_x) phase and the WSi_2 phase at a fixed annealing temperature. On the other hand, when the oxygen (or ammonia) partial pressure has been fixed, it is perfectly possible to control the reacted silicide thickness by varying the annealing temperature. Thus the W silicide process can be optimized by adjusting two free parameters: the partial pressure of the reactive atmosphere and the annealing temperature. For the experimental study silicon wafers with 600Å SiO_2 on the top were used. By reactive ion etching (RIE) two reverse patterns were obtained: either 40µm wide silicon lines with 4µm wide SiO_2 spacers or 4µm wide Si lines with 40µm wide SiO_2 spacers. Over the whole patterned wafer a 50nm thick W layer was sputtered. Residual vacuum values of a few 10^{-8} Torr were reached in the sputtering system before starting the W deposition. The W/silicon reaction was first studied on unpatterned Si wafers by using argon during thermal annealing. At 700°C the reaction is complete only for annealing times of about one hour, but at 750°C the annealing time is reduced to less than a quarter of one hour. Annealings under reactive atmospheres of oxygen and ammonia were then performed using patterned and unpatterned samples at annealing temperatures in the 700°C , 1000°C range and for annealing times much greater than necessary for a complete reaction of the W layer with the silicon. The patterned samples were observed by SEM and X ray diffraction, the unpatterned samples by RBS, nuclear reaction and X ray diffraction.

SEM observations

The photographs shown in Fig 1 and 2 correspond respectively to thermal annealing with oxygen and ammonia. As the SiO_2 spacers are only 60nm thick any lateral silicide formation of this order of magnitude over such spacers can easily be observed. Figure 1a shows the silicide grown at 850°C for 4mn, by using dilute oxygen and after chemical etching of WO_x . The silicide is perfectly aligned on the silicon line and no lateral silicide formation over the SiO_2 surfaces is observed. Fig 1b shows the edge of a SiO_2 line at the boundary with a silicide area. The silicide process has been well controlled. Fig 2a shows cross sections of patterned samples annealed at 850°C for 4mn under dilute NH_3 . The view in Fig 2a has been taken before chemical etching of WN_x formed on SiO_2 . The difference in the thickness of the deposited layer either over the SiO_2 surface or over the Si surface underlines the formation of two different phases over these two different surfaces. The photograph of Fig 2b shows the patterns after chemical etching of WN_x . Here also the W silicide process has been well controlled.

Fig.1-SEM observation of self aligned silicide grown at 850°C, 4 mn, under oxygen
a-plane view
b-edge of a SiO₂ spacer ,60 nm thick, at the boundary with a silicide area

Fig.2-SEM cross sections of patterned samples annealed at 850°C, 4mn, under NH₃
a-before chemical etching
b-after chemical etching

R.B.S and nuclear reaction

Annealing under NH₃ at atmospheric pressure (Fig 3):

In Fig 3a the squares correspond to thermal annealing at 700°C for one hour. Tungsten and silicon have not reacted. The corresponding nitrogen profile in Fig 3b obtained using the nuclear reaction $^{14}\text{N}(d,\alpha)^{12}\text{C}$ shows two peaks localised at the free surfaces of the sample ($4\text{E}16 \text{ at/cm}^2$ dose) and the W/Si interface ($3.1\text{E}16 \text{ at/cm}^2$ dose).

The crosses in Fig 3a are obtained when annealing at 750°C for one hour. A $\text{WN}_{0.7}$ compound has been found on the top of the layer, followed by a thick sublayer of unreacted W. The corresponding N profile shows a peak ($4\text{E}16 \text{ at/cm}^2$) localised at the W/Si interface. By increasing the temperatures for isochronal annealings the amount of N into W increases slowly. Finally a homogeneous WN stoichiometry is found when annealing at 900°C and above. From RBS and nuclear reaction, observations two important conclusions can be reached

1) N diffuses through the layer without precipitate WN_x compounds for annealing temperatures up to 750°C. As N solubility in W is very low, the N diffusion must occur at the W grain boundaries. The driving force could be the formation at the Si surface of SiN_x compounds thermodynamically favorable with regard to WN_x compounds.

2) The growth kinetics rate for the WN_x phases are low compared with the WSi_2 kinetics

3) As a result of the preceding remarks, it appears to be the rapid accumulation of N at the W/Si interface which blocks the silicon diffusion and impedes the WSi_2 formation.

Fig.3 a-RBS spectra of W after annealing under atmospheric pressure
b-corresponding N profiles by nuclear reaction

Annealing under oxygen atmospheric pressure:

The W is completely oxidized and forms the WO_3 phase for annealing temperatures above 500°C . The RBS spectrum in Fig 4 corresponds to thermal annealing at 400°C for one hour. The corresponding oxygen profile has been obtained using the nuclear reaction ($^{16}\text{O}(d,\alpha)^{14}\text{N}$). A WO_3 layer is found at the free surface covering an oxygen free unreacted W layer. Moreover, not any oxygen peak at the W/Si interface has been observed. The W behaviour with oxygen is found to be very different from the behaviour found with N:

- 1) Free oxygen does not diffuse through the W layer to accumulate at the W/Si interface
- 2) The WO_3 phase forms at temperatures as low as 400°C , and its growth kinetics is very fast compared with the WSi_2 growth kinetics
- 3) As a result, it is the rapid formation of WO_3 which impedes the formation of WSi_2 .

Fig.4 a-RBS spectrum of W after annealing under oxygen at atmospheric pressure
b-corresponding O profile obtained by nuclear reaction

X ray diffraction measurements and resistivity measurements have also been performed and the results confirm the RBS observations.

3-CONCLUSION

Self aligned W silicide formation has been controlled by using oxygen and ammonia as reactive annealing atmosphere. After furnace thermal annealing, W nitride and W oxide can be selectively removed using a chemical etching which leaves only the WSi_2 phase. Moreover, with respect to important processing aspects -dopants redistribution between WSi_2 and poly or monocrystalline Si allowing to form very shallow junctions below silicided contacts, compatibility of the silicide with a first W C.V.D. interconnection level/3/- WSi_2 presents a very interesting behaviour making it very attractive for self aligned silicide processes.

REFERENCES

- /1/ M. E. Alperin, T. C. Hollaway, R.A.Haken, C.D.Gosmeyer, R.V.Karnaugh and W.D.Parmantie, IEEE Trans .Electron devices ED_32,141,1985
- /2/G.Bomchil, G.Goltz and J.Torres, Thin Solid Films, 59, 1986
- /3/F.C.Shone, K.C.Saraswat and J.D.Plummer, IEDM Technical Digest, 407, 1985