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Interdiffusion and Compound Formation in the Mo/Si Thin Film Metallization System

Houria Benkherbache and Abdelali Merabet
Laboratoire de Physique et Mécanique des Matériaux Métalliques, D'O.M.P.,
Faculté des Sciences de l'Ingénieur, Université de Sétif, (19000) Sétif, Algerie

Abstract: In this study, we have used the silicon wafers. Before the deposit of film, the oxide layer has been removed by chemical cleaning. After, the thickness of 80 nm molybdenum layer has been deposited by electronic bombardment. The samples were heat treated at temperatures ranging from 500 to 700°C for different time duration under vacuum. We report here on the electrical characterization of the interdiffused and reacted Molybdenum-Silicon bilayered system by means of sheet resistivity measurements using four point probes. X-ray diffractometry were taken, in order to observe the formation of phases that occur at annealing conditions which cause drastic modifications in the sheet resistivity values.

Key words: Silicon, interdiffusion, silicide, X-ray diffraction, sheet resistance

INTRODUCTION

In this layers play an important role in nearly all the modern technology areas, in particular in microelectronics and in the manufacture of precise devices (Chopra, 1969; Kazmerski, 1980; Holland, 1965). In all practical application, it is required that the thin layer structure stay stable. However, we observe in general that a pronounced mutual diffusion (interdiffusion) or a phase formation (reaction) can be produced at low temperatures. That is why, the study of diffusion and reaction in solid state in the thin films has attached a particular attention in the recent years (PSIVC and TICSS, 1977; Poate *et al.*, 1978; Baglin and Poate, 1978). The remarkable result of these studies is that the interdiffusion and the reaction in thin layers are generally are produced at low temperature (PSIVC and TICSS, 1977; Poate *et al.*, 1978) and are presented under 2 aspects: Firstly, as a non-desirable phenomenon leading after phase formation at the physical and mechanical property degradation, secondly as a desirable phenomenon that permits the complex metallic separation formation in the integrated circuits and bringing possible the supraconductor film elaboration at relatively high temperatures, contacts and diffusion barriers and so on (Poate *et al.*, 1978; Baglin and Poate, 1978, 1980). The silicide of Mo, Ta, Ti, W have been broadly studied because of their compatibility with the VLSI process. It exists a big difference of silicide layers resistivity (13-110 μΩcm), however all after an important reduction of the resistivity comparing to polysilicon (500-1000 μΩcm) (Berrebah, 1994).

MATERIALS AND METHODS

The used substrates during this research have been obtained by the Czochralski grown method, oriented according to the direction (111) of P type and of resistivities studded between 60 and 80 μΩcm. Before the molybdenum metallic film deposition, the native oxide layer has been removed by HF followed by RCA cleaning. The molybdenum layers are obtained by evaporation under vacuum ($\approx 10^{-6}$ Torr) with electron canon, on the silicon substrates heated at 100°C. The rate condensation of molybdenum layers is about 80 nm. The samples have been thermally treated under vacuum in quartz type in temperature range (500-700°C) for different times. The annealing temperature is measured and controlled with the help of thermocouple. Then the samples are analyzed by the X-ray diffraction (vertical diffractometer with a copper radiation CuKα, a filter of Ni) and the measure of electrical resistance by the four point's method.

RESULTS AND DISCUSSION

The sample electrical characterization is effected by the measured setting realized in the department based upon the four points probe method (Valdes, 1954; Vapaille, 1990; Smits, 1958). With these four metallic points equidistant and aligned, we realize the punctual contacts. An electrical current I go through the external two points and we measure the potential difference V between those of middle. Two configurations are generally adopted for pointes, the disposition in line or square. We have chosen the line disposition (Fig. 1). This technique needs then

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Corresponding Author: Houria Benkherbache, Laboratoire de Physique et Mécanique des Matériaux Métalliques, D'O.M.P., Faculté des Sciences de l'Ingénieur, Université de Sétif, (19000) Sétif, Algerie

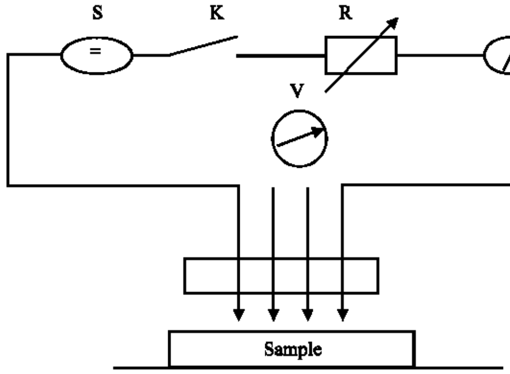

Fig. 1: Points disposition of aligned measure

simply a current source (we impose I) and a voltmeter (we measure ΔV). It constitutes a rapid test of layers. This technique permits to measure the active electric portion. We measure the ratio ΔV/I. This ratio can be related at a material resistance. The value R is given by: $R_1 = C.\Delta V/IC$. is corrected factor. Finally, the square resistance in our case is given by the following relation: $R_1 = 4.53\ \Delta V/I$.

The measure of sheet resistance in function of temperature in the range of (500-700°C) with a path of 50°C for different annealing duration (Fig. 2), show in general a rapid decrease of the resistance when time increases, for the five temperatures. The sheet resistance measured on then non annealing sample is of 25 Ω/1. The sample exam of measures at 500°C show a slight decrease of resistance by increasing the annealing time and tend to a constant value, that allow us supposing, that the electrical activity is total beyond 60 min and the saturation value is around of 1,75 Ω for the four other temperatures (550-700°C) the variation of the resistance shows a brutal decrease. Then, this resistance decreases slightly with time and its saturation value is of 1.6 Ω for 550°C at 45 min, it is of 1.5 Ω for 600°C/35 min and 1.35 Ω for 650°C/25 min. However, for 700°C, we observe the saturation at 20 min and its value is about 1,2 Ω. The resistance curves become more and more selected when the temperature more and more increases. This phenomenon shows that the electrical activity is more rapid for high temperatures. These results show the interest of use of the Molybdenum. And as we can see, these silicides present a low electrical resistivity to the polysilicon (Gontrand *et al*., 1993; Seto, 1975) and also for the silicide of chromium (Merabet, 2004).

The X-ray diffraction is an analysis method as well quantitative as qualitative which permits to characterize the metal layer structure (Mo) deposited on the silicon substrate to identify the nature and to determine the phases crystallography structure that are formed at the Mo/Si interface during rapid thermal annealing. The X-ray crossing a crystalline substance is diffused by these atoms. The diffusion is made on the atom electronic layers which become after that the sources of X-rays waves. The interference of these waves give birth to a diffraction picture that its intensity is reinforced in such directions (maximum of intensity diffraction peak). The intensity and the position of maximum are determined by the atomic structure of the considered substance. The nature and the proportion of many elements included in the sample can be determined by the angle measurement of diffraction peak and also their intensity. The angular position is calculated by basis formula of Bragg interreticular distance and of the wave length of the used radiation (Eberhart, 1976). In the range of annealing temperature of (500-700°C) and according to phase equilibrium diagram of binary system Mo/Si (Hansen, 1985) four intermetallic composed (silicide of molybdenum) (h-$MoSi_2$, t-$MoSi_2$, Mo_5Si_3 and Mo_3Si) should be formed. The Fig. 3 presents

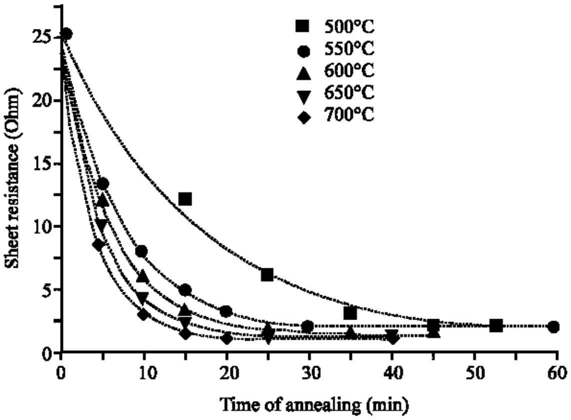

Fig. 2: Sheet resistance in function of time for different temperatures

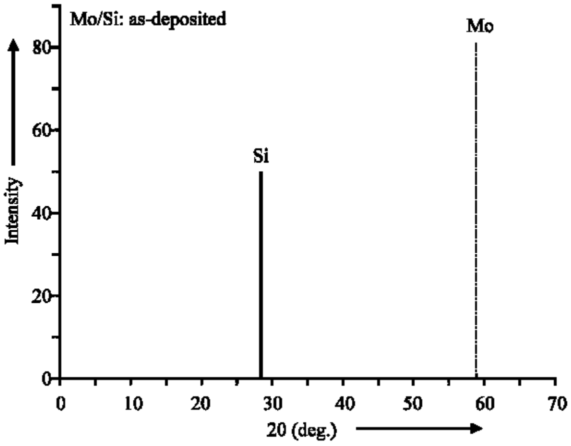

Fig. 3: X-ray diffraction spectrum of the non annealing sample

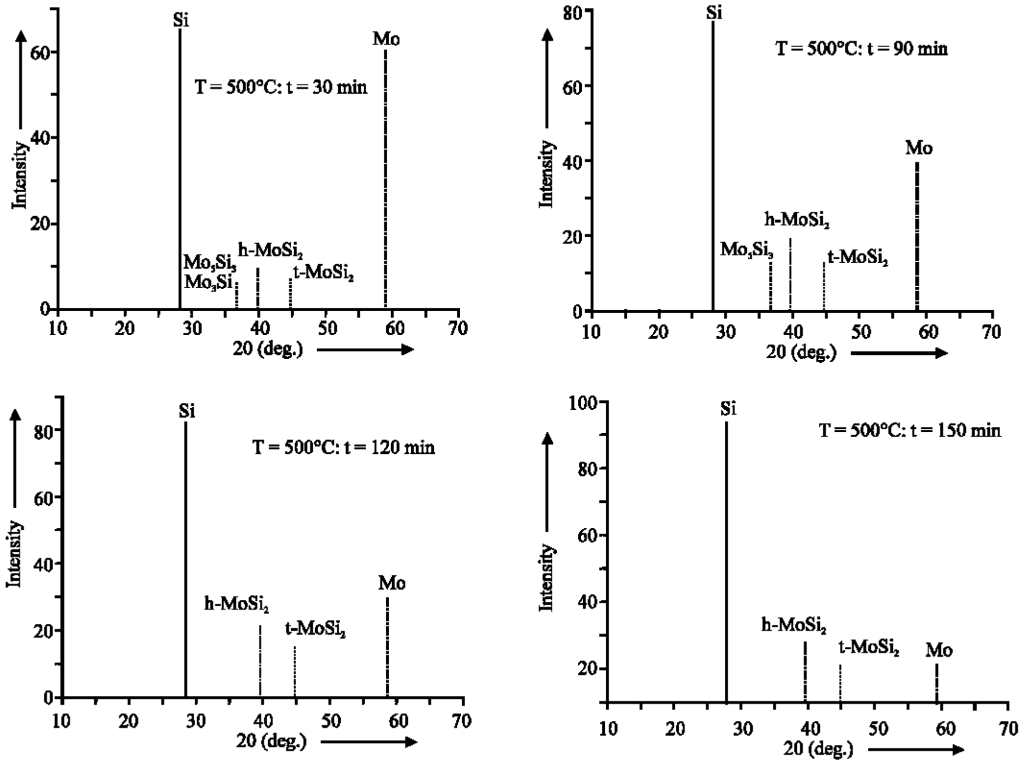

Fig. 4: The diffraction spectrum of annealing at 500°C samples for different time

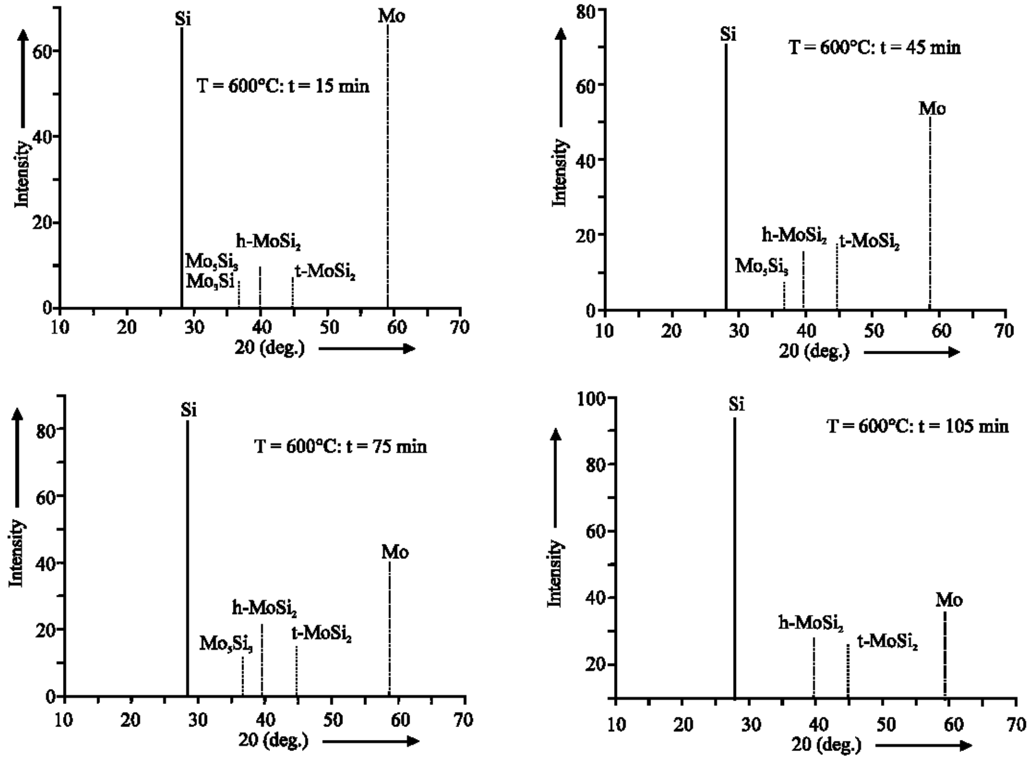

Fig. 5: The diffraction spectrum of annealing at 600°C samples for different time

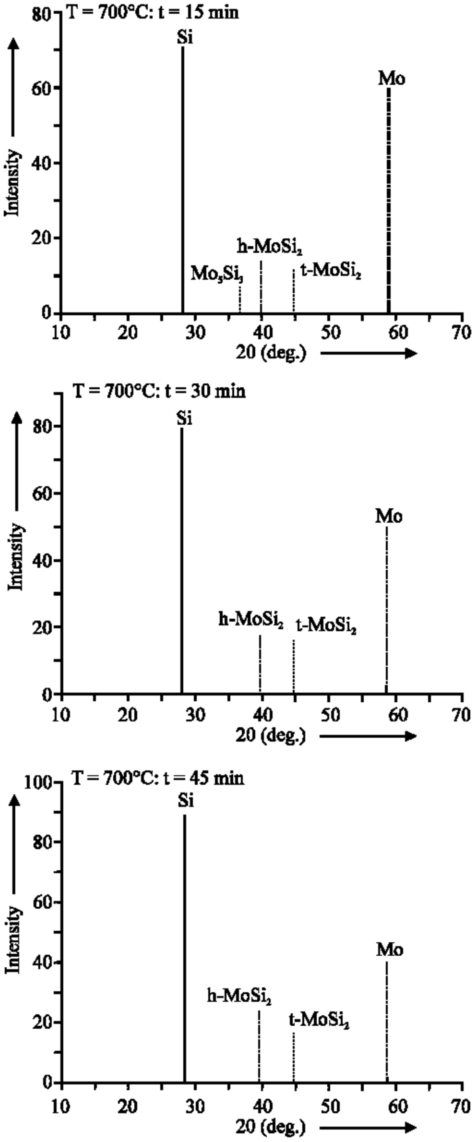

Fig. 6: The diffraction spectrum of annealing at 700°C samples for different time

the X-ray diffraction spectrum of the referred sample molybdenum on the silicon substrate (111), before annealing. This latter shows the only presence of Si and Mo peaks, which confirms that none interdiffusion is produced during the deposition.

Figure 4 and 5 illustrate the diffraction spectrum of annealing samples at 500 and 600°C, for time of 15 at 150 min. The phases (h-MoSi$_2$, t-MoSi$_2$, Mo$_5$Si$_3$ and Mo$_3$Si), expatiated are appeared near of molybdenum and silicon reflection. The molybdenum intensity decreases with the temperature increase, this fact permits to confirm the partial consummation of the molybdenum layer. The prolongation of time shows the three phase growth (h-MoSi$_2$, t-MoSi$_2$, Mo$_5$Si$_3$ and Mo$_3$Si) and the missing of the compound Mo$_3$Si from 75 min. The extension of annealing leads the other phase missing Mo$_5$Si$_3$ from 120 min at 500°C and from 105 min for 600°C.

The annealing at 700°C (Fig. 6), shows the presence of three phases (h-MoSi$_2$, t-MoSi$_2$, Mo$_5$Si$_3$ and Mo$_3$Si) and the non formation of Mo$_3$ Si. After 30 min of annealing, we remark the disappearing of two phases the most rich in molybdenum, that is: Mo$_3$Si and Mo$_5$Si$_3$. The conversion process of the complete molybdenum layer in silicide is blocked, even for those of high temperatures and the lengthy time. The molybdenum layer does not react totally. That is to say that exist a diffusion barrier at the Mo/Si interface which shows down the silicide kinetic growth.

CONCLUSION

The obtained results shows that the conventional thermal annealing under vacuum in the temperature range 500-700°C leads to the beginning of annealing at the formation of four phases (h-MoSi$_2$, t-MoSi$_2$, Mo$_5$ Si$_3$ and Mo$_3$ Si). The prolongation of time leads the disappearing of two phases the more rich in molybdenum (Mo$_5$ Si$_3$ and Mo$_3$ Si) and the growth of the two others. The molybdenum layer does not react totally even for lengthy time.

REFERENCES

Baglin, J.E.E. and J.M. Poate, 1978. Thin Film Phenomena-Interfaces and Interactions. Electrochemical Society, New York.

Baglin, J.E.E. and J.M. Poate, 1980. Thin Film Interfaces and Interactions. Electrochemical Society, New York.

Berrabah, M., 1994. Thèse de Doctorat, INSA de Lyon (France), pp: 132.

Chopra, K.L., 1969. Thin film Phenomena, Mc Graw-Hill, New York.

Eberhart, J.P., 1976. Méthodes Physiques d'Etudes des Minéraux et des Matériaux Solides, Ed. Doin, Paris.

Gontrand, C., A. Merabet, S. Kreiger-Kaddour, C. Dubois and J.P. Vallard, 1993. J. Elec. Math., 22: 135.

Gontrand, C., A. Merabet, B. Semmache, S. Kreiger-Kaddour, C. Bergaud, M. Lemiti, D. Barbier and A. Laugier, 1993. Semicond Sci. Tech., 8: 155.

Hansen, M., 1985. Constitution of Binary Alloys, (Ed.), Graw-Hill, New York..

Holland, L., 1965. Thin Film Microelectronics, Chapman and Hall Ltd., London.

Kazmerski, L.L, 1980. Polycristalline and Amorphous Thin films and Devices. Academic Press, New York.

Merabet, A., 2004. Materials Science and Engineering B, 114-115 C, pp: 214.

Poate, J.M., K.N. Tu and W. Mayer, 1978. Thin Films-Interdiffusion and reactions. Wiley Interscience, New York.

Proceedings of the Seventh International Vacuum Congress and the 3rd International Conference on Solid Surfaces, Vienna-Austria, 1977.

Seto, J.Y.W., 1975. J. Applied Phys., 46: 5247.

Smits, F.M., 1958. The Bell System Technical J., pp: 711.

Valdes, L.B., 1954. Proc. IRE., 42: 420.

Vapaille, A. and R. Castagne, 1990. Dispositifs et circuits intégrés semiconducteurs. Paris: Dunod, pp: 572.