

Mesotaxy by nickel diffusion into a buried amorphous silicon layer

Yu. N. Erokhin

Institute of Microelectronics Technology, Russian Academy of Sciences, Chernogolovka, 142432 Moscow region (Russia)

R. Grötzschel

Central Institute für Kernforschung, Rossendorf, Dresden (FRG)

S. R. Oktyabrsky

P. N. Lebedev Physical Institute, 53 Leninsky prospect, 117924 Moscow (Russia)

S. Roorda* and W. Sinke†

FOM-Institute for Atomic and Molecular Physics, Kruislaan 407, Amsterdam 1098SJ (Netherlands)

A. F. Vyatkin

Institute of Microelectronics Technology, Russian Academy of Sciences, Chernogolovka, 142432 Moscow region (Russia)

Abstract

A novel method to produce a buried epitaxial silicide in silicon is described. Metal atoms are deposited onto the surface of a piece of crystalline silicon (c-Si) which contains a buried amorphous silicon (a-Si) layer in the "as-implanted" state. Prolonged heating at 350 °C leads to diffusion of metal atoms through the thin c-Si top layer followed by a chemical reaction with the buried a-Si, forming buried epitaxial silicide islands. These islands then move through the a-Si layer, leaving behind epitaxially crystallized silicon.

1. Introduction

Transition metal silicides have a wide range of applications in electronics [1]. In most cases silicides are formed by interfacial reactions between metal films and silicon substrates. The development of three-dimensional integration technology and novel microelectronic devices has encouraged activity in the field of buried conducting layer formation [2, 3]. Silicides are the most promising material for this purpose. Recently, metal ion implantation and molecular beam epitaxy have been employed to produce structures with one or two single-crystal buried silicide layers [4, 5]. However, both these methods have the same disadvantage—low efficiency of the process. In this paper we

describe a method for the formation of buried silicide which requires less implanter time.

It is known that the energy barrier for the metal–silicon reaction is lower for amorphous silicon (a-Si) than for crystalline silicon (c-Si) [6, 7]. This means that the temperature necessary to initiate the reaction with a-Si might be lower than in the case of c-Si. de Reus *et al.* [6] showed that epitaxial NiSi₂ can be formed during relatively low temperature annealing by nickel diffusion through an amorphous Ni–Zr film in the Ni/a-Ni₆₀Zr₄₀/c-Si(111) structure. The high diffusion coefficient of nickel plays a key role in the process. We expect that if the diffusion of metal atoms from the film deposited onto the surface of the structure of crystalline silicon with the buried amorphous layer is high enough at the minimum temperature necessary for the metal reaction with amorphous silicon, silicide formation on the front amorphous–crystalline interface will be preferential.

The purpose of this work was to investigate the possibility of the formation of buried epitaxial silicide

*Present address: Université de Montréal, Département de Physique, Case Postale 6128, Succursale "A", Montréal, Qué. H3C 3J7, Canada.

†Present address: Netherlands Energy Research Foundation (ECN), PO Box 1, 1755 ZG Petten, Netherlands.

by metal atom diffusion from the surface to the buried amorphous layer during low temperature annealing.

2. Experimental details

Nickel was selected for study of the diffusion-limited formation of buried silicide. The choice was made because of the high diffusivity of this metal in silicon and was based on a solution of the one-dimensional diffusion equation taking into account the diffusivity and solubility of different elements in the temperature range 200–500 °C. Experimental samples were prepared in the following way. First the structures with buried amorphous layer were manufactured by 100 keV P⁺ ion implantation to a dose of 10¹⁵ cm⁻² in n-type (100) silicon wafers (7 × 10¹⁴ electrons cm⁻³). To create a sharp a-Si-c-Si interface, half of each wafer was preannealed at 450 °C in flowing argon for 1 h. Then a 100 Å nickel film was evaporated onto the surface of the samples under high vacuum conditions (2 × 10⁻⁶ Pa). Just before the metal deposition, all the samples were etched in 4% HF acid. After the metal evaporation, part of every sample (with preannealing or without it) was subjected to thermal annealing at a temperature from 200 °C to 500 °C for 15 min to 159 h in vacuum or in a dry nitrogen atmosphere. All the structures were prepared at the FOM-Institute of Atomic and Molecular Physics (Amsterdam, The Netherlands). Rutherford backscattering (RBS) studies were carried out at the Central Institute of Nuclear Physics (Rossendorf, F.R.G.). Electron microscopy studies and X-ray microanalysis were performed at the Lebedev Physical Institute in Moscow on the Philips CM-30 electron microscope at an accelerating voltage of 300 keV.

3. Results and discussions

Table 1 lists a summary of the RBS investigations of the nickel atom distribution in the surface region of the structures after thermal annealing. Only samples 7, 9 and 10 exhibit a buried metal-enriched layer.

Figure 1(a) shows the channelling and random spectra of sample 7. It is clear that significant nickel atom transport to the front c-Si-a-Si interface has already occurred at a temperature as low as 350 °C. However, this is only true for samples which have not been exposed to preliminary thermal annealing just after ion implantation.

As seen from the spectra in Fig. 1(a), the accumulation of nickel atoms at the c-Si-a-Si boundary takes place in a regular (epitaxial) manner relative to the silicon lattice, the local maximum of the nickel concentration profile being in the a-Si region. A crystalline silicon layer about 400 Å thick still remains between the a-Si and the structure surface. Despite the low annealing temperature, the formation of the buried silicide is accompanied by recrystallization of part of the amorphous silicon. This is in agreement with ref. 7.

The difference in silicide formation processes of the samples exposed to preliminary annealing and the as-implanted samples can be the result of at least two reasons. Firstly, the higher density of nickel atoms at the c-Si-a-Si interface in the untreated samples may be due to radiation damage which has accumulated in the c-Si region during ion implantation and leads to enhanced diffusion. However, the heat treatment at 350 °C for 15 min (*i.e.* approximate lifetime of radiation defects near the surface [8]) does not lead to the formation of buried silicide; this requires much more prolonged annealing. This means that radiation damage accumulated in the surface c-Si layer does not play a key role in the formation of buried silicide.

TABLE 1. Annealing regimes used for metal/c-Si/a-Si/c-Si(substrate) structures

Sample	Metal	Preannealing	Main annealing			Buried silicide presence	
			Temperature (°C)	Duration (h)	Ambient	Presence	Epitaxial (+) or not (-)
1	Ni	-	200	159	Vacuum	-	-
2	Ni	+	200	159	Vacuum	-	-
3	Ni	-	250	43	N ₂	-	-
4	Ni	+	250	43	N ₂	-	-
5	Ni	-	350	0.25	Vacuum	-	-
6	Ni	+	350	0.25	Vacuum	-	-
7	Ni	-	350	43	Vacuum	+	+
8	Ni	+	350	43	Vacuum	-	-
9	Ni	-	200	43	Vacuum	+	-
10	Ni	+	500	1			
			200	43	Vacuum	+	-
			500	1			

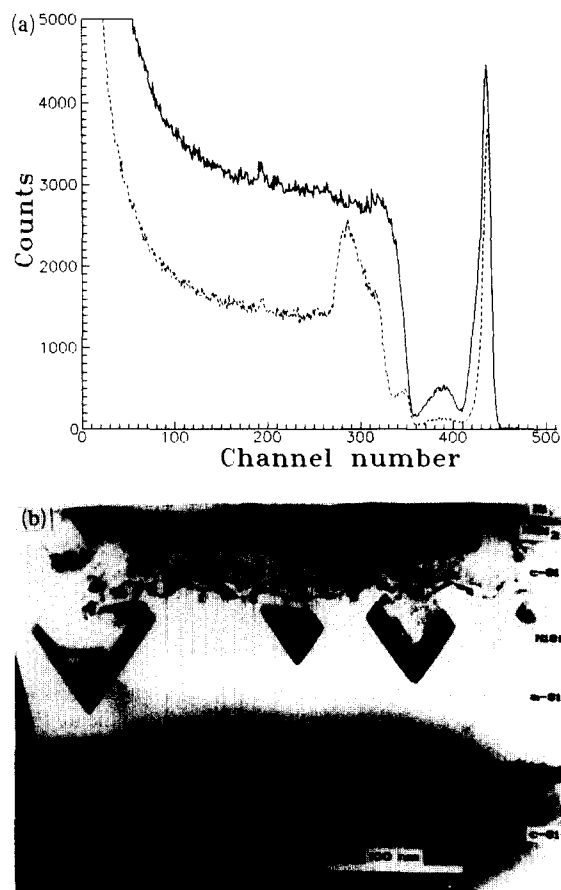


Fig. 1. (a) 1.4 MeV $^4\text{He}^+$ RBS channelling and random spectra of Ni(100Å)/c-Si/a-Si/c-Si(substrate) structure subjected to vacuum annealing at 350 °C for 43 h (sample 7), scattering angle 115°. (b) Cross-section transmission electron microscopy bright-field image in [110] orientation and selected area diffraction patterns of the sample in (a).

Secondly, the difference considered above may be caused by a change in the structural state of the amorphous silicon layer. It has recently been shown [9] that thermal annealing of an a-Si layer formed by ion implantation results in structural transition from an "as-implanted" to a "well relaxed" condition with lower free energy. Our experimental data show that the formation of buried silicide is accelerated when nickel atoms interact with a-Si in the "as-implanted" structural state. In addition, this idea is confirmed by the results for Ni/c-Si/a-Si structures which were heat treated at 500 °C. In this case we observed no epitaxial silicide formation, although nickel atoms accumulated at the c-Si–a-Si interface but at a smaller concentration than for annealing at 350 °C.

Thus we postulate that the probable reason for the difference in silicide formation processes is the accelerated solid phase reaction of nickel with a-Si in the "as-implanted" state. This leads to an enhancement of

nickel atom diffusion through a-Si since the drain of nickel atoms and hence the nickel concentration gradient increases.

The detailed structure of sample 7 was investigated by analytical electron microscopy. A bright field image of a cross-section of the structure is shown in Fig. 1(b). Two regions of silicide crystallization can be seen distinctly: the first is at the surface of the silicon wafer under the nickel layer, and the second is at some depth in the a-Si layer near the c-Si–a-Si interface. In both cases the silicide crystallites grow epitaxially with the substrate, their electron diffraction patterns coincide (allowing for double diffraction from silicon) as shown in the inset to Fig. 1(b). Thus there is no doubt that the silicide crystallizes in the NiSi_2 f.c.c. structure which is isoperiodic (with misfit 0.4%) and almost isomorphic with silicon.

To confirm the growing process of NiSi_2 cross-sectional images of the structure are shown in Fig. 2(a) using transmitted electrons and characteristic X-rays for nickel and silicon.

As can be clearly seen from the pictures, the front-line of crystallization of the nickel disilicide proceeds parallel to the $\langle 111 \rangle$ directions, resulting in a characteristic shape of the NiSi_2 layer as a set of protrusions faceted with $\langle 111 \rangle$ planes with the lowest free energy. This type of NiSi_2 crystallization has been repeatedly observed before at the Ni–c-Si interface (see for example ref. 10), but the diffusion-limited growth at the c-Si–a-Si interface exhibits some important peculiarities. The appearance of a back crystallization frontline is apparently the main difference. During growth the silicide layer is displaced as a whole into the a-Si. As the NiSi_2 layer passes through the amorphous region the latter becomes single-crystal with the orientation of the parent silicon. This is clearly confirmed by Fig. 2(b) where a high-resolution image of the c-Si–a-Si interface is presented. The dark region shows the growth form of NiSi_2 faceted with [111] planes from a-Si as well as c-Si. The symbol R denotes the silicon region recrystallized by the spreading of the silicide frontline.

The observed silicide formation process implies the following scheme. After the formation of initial silicide atomic layers at the c-Si–a-Si interface, further growth occurs at the interface with a-Si resulting from the diffusion of metal atoms through the silicide layer. Two sources of nickel atom diffusion appear: the first is the surface nickel film, and the second is silicide decomposition at the NiSi_2 –c-Si boundary. Such a process with simultaneous growth of the silicide at one facet and decomposition at the other is quite probable from a thermodynamic point of view. The free energy of the whole system is diminishing since its change is defined to the first approximation by the difference in volume of c-Si and a-Si.

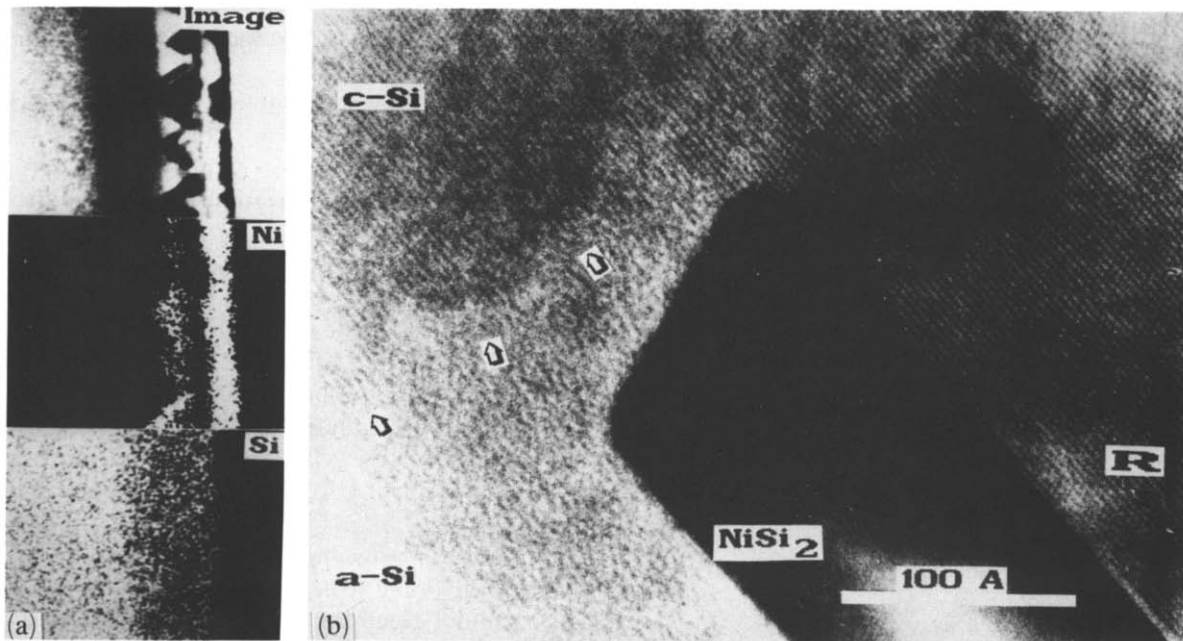


Fig. 2. (a) Scanning electron transmission images of the sample in Fig. 1(a): top, using transmitted electrons; middle, using characteristic X-rays of nickel (line $K\alpha = 7.47$ keV) and bottom, silicon (line $K\alpha = 1.74$ keV). (b), High resolution $\{110\}$ image, arrows indicate the interface between c-Si and a-Si, R is recrystallized silicon.

4. Conclusions

A new method for the fabrication of buried epitaxial silicides in silicon has been presented. Nickel was deposited on top of a c-Si wafer which had first been ion implanted until a buried a-Si layer had formed. Prolonged annealing at a temperature of 350 °C leads to the formation of epitaxial NiSi_2 islands, buried within the silicon matrix. The islands move through the buried layer, consuming a-Si and leaving c-Si behind.

Acknowledgments

It is a pleasure to thank F. W. Saris for helpful and stimulating discussions and J. R. Liefing for the buried a-Si samples. Work at FOM was financially supported by Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) and the Stichting Technische Wetenschappen (STW).

References

- 1 S. P. Murarka, *Silicides for VLSI Applications*, Academic Press, Orlando, FL, 1983.
- 2 R. T. Tung, J. M. Poate, J. C. Bean, J. M. Gibson and D. C. Jacobson, *Thin Solid Films*, 93 (1982) 77.
- 3 R. T. Tung and F. Schrey, *Mater. Res. Soc. Symp. Proc.*, 122 (1988) 559.
- 4 A. E. White, K. T. Short, R. C. Dynes, J. P. Garno and J.M. Gibson, *Appl. Phys. Lett.*, 50 (1987) 95.
- 5 A. Vantomme, M. F. Wu, G. Langouche, K. Maex, H. Vanderstraeten and Y. Bruynseraede, *Proc. 7th Int. Conf. on Ion Beam Modification of Materials, Knoxville, TN, 1990*, in the press.
- 6 R. de Reus, H. C. Tissing and F. W. Saris, *J. Mater. Res.*, 5 (2) (1990) 341.
- 7 R. C. Cammarata, C. V. Thompson, C. Hayzelden and K. N. Tu, *J. Mater. Res.*, 5 (10) (1990) 2133.
- 8 L. S. Smirnov (ed.), *Radiation Technology of Semiconductors*, Nauka, Novosibirsk, 1980 (in Russian).
- 9 S. Roorda, S. Doorn, W. C. Sinke, P. M. L. O. Scholte and E. van Loenen, *Phys. Rev. Lett.*, 62 (1989) 1880.
- 10 L. J. Chen, J. W. Wagner, K. N. Tu and T. T. Sheng, *Thin Solid Films*, 93 (1982) 91-97.