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Silicide Formation on Polycrystalline Silicon by Direct Metal Implantation

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Increases in component packing densities have led to decreasing lateral and vertical dimensions within integrated circuits. Reduced cross-section conductors can have unacceptably high resistances which leads to increased signal propagation delays. This is especially true for lower level conductors, e.g., source-drain regions and polycrystalline-silicon (poly-Si) gates and gate level interconnections. Silicon (or poly-Si) which has been doped with materials such as phosphorus or arsenic has a relatively high sheet resistance (a typical minimum for poly-Si is 20 Ω/\Box). Hence, various low-resistivity silicide (and polycide) schemes have been developed (1).

The lowest resistivity silicide and polycide layers are generally formed by depositing a transition metal on the silicon or poly-Si. A thermal step then follows in which interdiffusion of the metal and underlying silicon occurs. However, control of these diffusion processes can be difficult to attain, especially if a diffusion barrier is present (e.g., a native oxide on the silicon). Similar problems arise when a "polycide" gate is formed by sputtering a complete silicide layer onto a buffer layer of poly-Si, as some interdiffusion between the two layers is still required to establish a good electrical contact. Uneven interdiffusion will occur when poly-Si is involved in the reaction due to high grain boundary diffusivity effects. This lack of control of material distribution will result in the formation of nonuniform silicide layers.

This paper discusses an alternative method of silicide formation on poly-Si which allows a higher degree of control than conventional polycide formation methods. The technique involves the direct implantation of high doses of transition metal ions into the poly-Si layer, followed by a transient annealing step.

Direct Metal Implantation

Direct ion implantation of high doses of transition metal ions into silicon to form silicides has been studied by various researchers (2, 3). This past work involved single-crystal silicon, although some high-dose metal implants into poly-Si have also been attempted (4). Buried, single-crystal CoSi₂ layers have been produced in single-crystal silicon substrates (2, 5); this is one of the unique advantages of the technique. However, there are other advantages related to the controlled formation of polycides on poly-Si.

Direct implantation of the transition metal, followed by a rapid annealing cycle, dispenses with the metal-on-silicon reaction and allows a high degree of control over the amount of metal introduced and the distribution of the resulting silicide. It also overcomes the effects of diffusion barriers as the metal ions penetrate into the silicon, passing through any surface layers which may be present. High doses of metal ions are required to create the desired silicide phase, which is typically the disilicide due to its low resistivity. Since the atomic density of silicon is approximately 5×10^{22} cm⁻³, this implies that in order to create the disilicide, the concentration of the metal must be 2.5×10^{22} atoms cm⁻³ over the silicide forming region to produce a 1*M*:2Si ratio. For any chosen metal and implant energy (producing a particular projected range and straggle), a critical dose will exist, below which there will be an insufficient local concentration of metal in the silicon to form the desired phase at any point in the distribution. Doses larger than the critical dose will allow silicide formation (after the transient annealing process), the silicide layer thickness being determined by the dose and the straggle.

The critical dose for the disilicide case may be estimated by assuming a Gaussian postimplant metal distribution and calculating the dose necessary to produce a metal concentration of 2.5×10^{22} atoms cm⁻³ at the peak. Doses higher than the critical dose will then produce a layer, throughout which the concentration of metal is greater than 2.5×10^{22} cm⁻³ (Fig. 1). For example, if a particular metal ion has a projected range of 160 nm and a projected standard deviation of 63 nm in silicon, and if we assume a simple Gaussian distribution, the necessary dose to produce 2.5×10^{22} cobalt atoms cm⁻³ at the peak is approximately 4×10^{17} cm⁻². Unfortunately, this method is only approximate due to factors such as sputtering and the change in projected range during implantation due to the increasing metal concentration in the substrate (both of which are discussed later in this paper). These factors tend to increase the local metal concentration so that if we start with our critical dose calculation method, we still will not fall below the minimum desired metal concentration.



Fig. 1. Schematic diagram of Gaussian implant profile showing region of 1M:2Si average.

Table I. Projected range and straggle of Co into Si and Co into
1Co:2Si substrate materials. The underlined energies are
those used in this study

		d:			
	<u> </u>	0 51	Co into ICo:2Si		
Energy (keV)	Projected range (nm)	Straggle (nm)	Projected range (nm)	Straggle (nm)	
20	17	8	9	3	
40	29	14	16	5	
60	41	19	22	7	
80	53	24	29	9	
100	65	29	35	11	
120	77	34	42	12	
140	90	39	49	14	
150	96	41	52	15	
160	102	43	55	16	
180	115	48	62	17	
200	128	52	69	19	
220	140	57	76	20	
240	153	61	83	22	
250	160	63	87	23	
260	166	65	90	23	
280	179	70	97	25	
300	192	74	104	26	
320	206	78	110	28	
340	219	82	118	29	
350	225	83	121	30	
360	232	85	125	31	
380	246	89	132	32	
400	259	93	139	33	

Implantation and Annealing Results and Discussion

The metal chosen for the implants was cobalt as it forms a stable, low-resistivity disilicide and as such is becoming more frequently studied for use in semiconductor applications (6, 7). One interesting property that cobalt has is that it will not take part in the reduction of silicon dioxide (as compared with titanium, the oxide of which can readily reduce SiO₂) (8). This is a distinct disadvantage if metal-onsilicon reactions are to take place, as a layer of native oxide on the silicon will effectively retard the silicide forming process. On the other hand, it will also mean that the gate oxide integrity will not be compromised by the presence of cobalt in a gate polycide structure. Thus, cobalt disilicide may be the ideal material for this purpose.

The calculated projected range and standard deviation for various cobalt ion energies are shown in Table I for implantation into Si and also into a 1Co:2Si substrate. Note that the range of Co in Si is almost twice that of Co in a 1Co:2Si material. A solid (sputter) source was used in the implantation equipment to create the Co⁺ flux (although it is possible to utilize a volatile cobalt halide source instead). The implants were performed into 400 nm thick undoped poly-Si layers deposited by LPCVD on SiO₂ grown on silicon substrates. The grain size of the poly-Si layer was in the order of the film thickness. No attempt was made to remove any native oxide layer on the poly-Si prior to implantation. This was thought to be the most severe test of polycide formation by the implant method.

The implant parameters are shown in Table II. Estimated critical doses were increased by 10% for implants 1-3 to ensure the formation of silicide layers which would be thick enough to be characterized by four-point probe and RBS. One double-critical dose (implant 4) and two subcritical doses (implants 5 and 6) were also used. All implants were performed on 10×10 mm areas in the centers of 20×20 mm samples cut from 3 in. substrates. Beam

Table III. Change in sheet resistance with number of annealing cycles for implant 4

Number of annealing cycles	1	2	3	4	5
Sheet resistance (Ω/□)	1.20	1.00	0.90	0.80	0.75

currents were kept to a minimum ($<10 \mu A$), and heatsinking was used to avoid substrate heating, i.e., all implants were performed at room temperature. This was done to minimize metal redistribution during implantation so that the true as-implanted profile could be examined. The loss of silicon due to sputtering was predicted for each case and is also shown in Table II. The calculated sputtering yield (of Si implanted with Co) ranged from 2 (at 150 keV) to 1.5 (at 350 keV) (9). Actual sputtering loss appeared to be a factor of two lower than expected (sputtering loss was measured by profilometer before annealing). The difference in predicted to actual sputtered thickness was primarily attributed to the reduction in sputtering due to the increasing surface concentration of cobalt. Note that any surface native oxide will be removed first by the sputtering process.

The sheet resistances (R_s) for the as-implanted cases (Table II) in all but the subcritical doses were comparable to doped poly-Si, although x-ray diffraction indicated that the poly-Si was heavily disordered. The high as-implanted sheet resistances are attributed to this disorder (implant damage).

To remove the implant damage to the layer while minimizing metal redistribution, transient annealing (using a scanned E-beam system) was used (10). Each standard annealing cycle lasted 20s, the final temperature of 950°C being reached after 10s. The "long" (10s) heating time was used to prevent thermal damage to the samples. After the beam was switched off, the temperature of the samples dropped to below 400° C in approximately one tenth of a second. Table II also shows the postanneal sheet resistances (after 1 cycle) and the calculated widths of the cobalt disilicide layers, assuming a silicide resistivity of 18 $\mu\Omega$ -cm (1) and negligible contribution from the subdisilicide regions created by the "tails" of the implant distributions. This assumption is valid as the tails will have a much higher resistivity than the low-resistivity disilicide. These layer thicknesses were also confirmed by RBS analyses (to be discussed). In implants 1 and 2, the sheet resistances remained constant after the first annealing cycle; however, the stable sheet resistance of 0.75 Ω/\Box for the double-critical dose case was obtained after five annealing cycles (Table III). X-ray diffraction showed that all layers had apparently returned in a polycrystalline state after annealing. The high sheet resistances of implants 5 and 6 were due to the lack of cobalt for the formation of a low-resistivity phase (Co is a poor dopant in Si).

The layers were analyzed using RBS (2 MeV He, detector at 70° to the sample surface). Three examples of pre- and postanneal spectra are shown in Fig. 2a and b (implant 1), 3a and b (implant 2), and 4a and b (implant 4). In Fig. 2a, the as-implanted metal resides near the surface (metal concentration is sufficient for disilicide formation) and is redistributed to a small degree by a single annealing cycle to

Table II. Sputtering loss, sheet resistance, and estimated silicide width implants 1-6

Implant no.	Dose (cm ⁻²)	Energy (keV)	Sputtering loss (predicted) (nm)	Sputtering loss (actual) (nm)	$R_{ m s}$ (as-implanted) (Ω/\Box)	$R_{ m s}$ (postanneal) (Ω/\Box)	CoSi ₂ Final width (nm)
1	2.8×10^{17}	150	120	50-60 60 80	110	4.3	50
3	$7.0 imes 10^{17}$	350	210	70-100	9.0	0.9	170
4	$7.0 imes10^{17}$	200	280	100-130	20	0.75	200
5	$2.0 imes10^{17}$ 7.0 imes10^{16}	350 350	60 20	50	850-1000 Off scale	70 Off scale	_



Fig. 2. (a, left) RBS spectrum of implant 1, as-implanted. (b, right) RBS spectrum of implant 1, postanneal

form a stable disilicide layer approximately 50 nm thick (Fig. 2b). Upon close inspection, the spectrum suggests that the postanneal silicide layer is slightly silicon rich. However, the sheet resistance indicates that the low-resistivity phase (the disilicide) has been formed. Diffusion or incorporation of the metal into the grain boundaries will almost certainly occur to some extent during the anneal, but RBS does not specifically show this. Therefore more material analysis work is required to determine if other phases are present and to reveal the detailed microstructure of the materials.

A similar situation is seen in Fig. 3a and b, only the final silicide layer is thicker (approximately 100 nm) due to the larger dose and higher energy. Note the presence of "tails" in the cobalt distributions which extend below the silicide forming region into the underlying poly-Si for both implants. Further annealing cycles have little effect on the silicide distribution (and sheet resistance, as seen before). However, a long-term furnace heat-treatment at 950°C for 30 min allowed some of the "tail" cobalt to diffuse toward the poly-Si/SiO₂ interface. Figure 4a shows the as-implant-

ed "double critical" dose case, in which there is potentially a sufficiently high local cobalt concentration at the surface after implantation to form the monosilicide phase. However, the monosilicide is not stable as after five annealing cycles and considerable redistribution. A disilicide layer of approximately 200 nm thick is formed and occupies most of the final film thickness (Fig. 4b). No appreciable redistribution occurs with further annealing cycles, indicating that the cobalt has been redistributed to produce the most stable phase. Note that in the critical dose cases (implants 1-3), an underlying layer which is essentially poly-Si remains, which means that the structures are basically polycides.

It is evident from the RBS spectra that the as-implanted profiles are not perfectly Gaussian in nature and the situation is not exactly as shown in Fig. 1. The "distortion" of the profiles is primarily due to the effects of sputtering and change of range which effectively compress the distributions and shift them toward the surface (the film will also become thinner due to sputtering). The relatively high sheet resistances of the as-implanted samples suggest that



Fig. 3. (a, left) RBS spectrum of implant 2, as-implanted. (b, right) RBS spectrum of implant 2, postanneal



Fig. 4. (a, left) RBS spectrum of implant 4, as-implanted. (b, right) RBS spectrum of implant 4, postanneal



Fig. 5. RBS spectrum of "optimized" implant. The smooth line is the **RBS** simulation.

if any disilicide is forming, it is essentially discontinuous or is limited to short-range order due to the high degree of implant damage. It is also clear that there can be considerable redistribution of metal even during short-term heating cycles (until a stable silicide phase is attained). Taking these effects into account, it should be possible to predict optimized implantation and annealing parameters which may be used to create an evenly distributed silicide layer.

A number of experiments were performed to determine a more optimal choice of parameters. Figure 5 shows such "optimized" situation. The implant dose was an 5×10^{17} cm⁻² and the implant energy 350 keV. This dose is actually slightly below our "critical" value (as discussed previously) for this energy, but the "profile compression" effect still results in an as-implanted distribution which has a Co to Si ratio very near to 1:2 over a region of a few hundred nm (prior to annealing). A 10s annealing cycle was then used to remove the implant damage with minimum metal redistribution. The maximum temperature of 950°C was reached after 10s at which point the beam was switched off. The sheet resistance of the postannealed sample was $0.9 \Omega/\Box$. Figure 5 shows the postanneal RBS spectrum. The smooth line is a superimposed "best fit" simulation of a 180 nm thick layer of CoSi₂ on our SiO₂covered substrates, the small peak at the silicon edge being due to a 50 nm thick surface layer which is silicon rich (1Co:5Si). As we can see, the simulation is extremely close to the actual spectrum, the main difference being that the "real" spectrum exhibits a "tail" of cobalt (due to the nature of the original implant distribution). Since the simulation represents an evenly distributed layer of CoSi₂, we may see that we have succeeded in creating such an even layer on poly-Si by use of our optimized parameters. The existence of the silicon-rich layer on the surface is also interesting as we have effectively "buried" our silicide layer by using a high-implant energy. This may have some advantages in the subsequent processing of our layers, e.g., the overlying silicon-rich layer will be a good silicon source in the oxidation of the structure.

Processing of the Implanted Polycides

As we may see from the above results, the implanted polycides exhibited stability for multiple short-duration annealing cycles. However, structure stability during other processing steps also had to be assessed. The films were oxidized in a wet oxygen ambient at high temperature (950°C) for 30, 60, and 120 min. Other samples were coated with a deposited oxide formed by the pyrolytic decomposition of silane and oxygen at low temperature (400°C) for 15 min. The latter process had no detectable effect on the cobalt distribution or the sheet resistance, indicating that the implanted polycide process is compatible with this type of low-temperature processing. However, the thermal oxidations produced large changes in Co distribution and sheet resistance. The thickness of the grown oxide was the same as that on control wafers of undoped/ unimplanted poly-Si, i.e., 460 nm for the 120 min case. RBS analyses showed that the oxide was actually relatively free of cobalt, but that considerable amounts of metal had piled up at the poly-Si/surface-oxide interface in all cases. The samples appeared mottled by optical microscopy, suggesting the presence of precipitates at this interface. The centers of the surface features/precipitates were separated by distances on the order of the recrystallized grain boundary size, approximately 1 µm. This was to be expected as excess cobalt in the grain boundaries or in the tails of the distribution will diffuse along the grain boundaries during an extended heat-treatment and arrive at the poly-Si surface. The sheet resistance of the samples oxidized for 120 min rose from about 1 to 50 Ω/\Box after oxidation. This was primarily attributed to the fact that this relatively long oxidation time results in the partial consumption of the silicide layer in order to provide silicon for the growing oxide. For this length of oxidation, the underlying poly-Si layer is essentially consumed.

Summary and Conclusions

An alternative method for the formation of polycide layers has been presented. The method involves the direct implantation of high doses of metal ions into the poly-Si, followed by a transient annealing cycle. The method overcomes the problems associated with metal-on-silicon or silicide-on-silicon interdiffusion reactions, such as retarded diffusion due to surface barriers or uneven diffusion due to the presence of grain boundaries in the poly-Si. Hence, the technique can provide a high degree of control over silicide distribution. Cobalt disilicide (polycide) layers have been produced by this method with sheet resistances below 1 Ω/\Box . Optimizing the implant and annealing parameters leads to evenly distributed silicide layers in poly-Si, although the tail of the implant distribution extends into the underlying silicon layer. Implant profiles are generally not Gaussian as the range of the ions changes, becoming smaller as the substrate becomes more metal rich during the implant. Also, sputtering of the silicon layer is not as high as expected, as sputter yield also decreases as the substrate becomes more metal rich. The material used in this study, cobalt, appears to diffuse rapidly in poly-Si during heat-treatment. Redistribution of the implanted metal occurs during the annealing cycles until a stable phase is formed. For Co in the presence of excess silicon, this stable phase is the disilicide. Some metal, probably from the tail of the distribution, is redistributed with further long-term heat-treatments to form surface precipitates.

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