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Preliminary communication

Chemical vapour deposition of metals and metal silicides on the internal surfaces of porous silicon *

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Abstract

Cobalt, cobalt monosilicide and rhenium thin films have been deposited on the internal walls of both n- and p-type porous silicon (PS) by metallo-organic chemical vapour deposition (MOCVD) at moderate temperatures and low pressure. Characterisation of the films by Rutherford Back-Scattering (RBS) showed penetration of Co, CoSi and Re into the pores to a depth of at least 2 μm, the concentration decreasing with increasing depth; NRA light element analysis revealed that substantial levels of oxygen and, to a lesser extent, carbon were present in the films.

Porous silicon was originally discovered by Uhlir in 1956 [1], but it is only within the last 8 years that the properties of this unique material have been intensively studied by a number of research groups. As one result, porous silicon (PS) has been used to produce silicon-on-insulator (SOI) high performance transistors [2], claimed to show enhanced performance over conventional CMOS devices. Recent exciting discoveries include the photoluminescence of porous silicon upon irradia-

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tion with blue or green Ar laser radiation [3] and its electroluminescence in the visible range [4], corresponding to a band gap well above that of bulk silicon. It is therefore possible to envisage silicon-based optoelectronic applications in the future.

We now report the use of MOCVD techniques to deposit metals and metal silicides on and within porous silicon. Such structures have many potential applications, particularly as buried conductors, but also as interconnects, barrier layers, and Schottky devices. Thin films of metal silicides are widely used in the manufacture of advanced semiconductor devices for VLSI technology [5]; the initial processing step normally involves deposition of a metal layer by sputtering, molecular beam methods, or plasma deposition, followed by high-temperature annealing, which yields the silicide by reaction with the substrate. Also metal silicides can be directly deposited at relatively low temperatures in a CVD process by using an appropriate organometallic precursor [6]. The only previous reports of a CVD process involving a metal-containing precursor and porous silicon are by Tsao *et al.* [7a] and Earwaker *et al.* [7b], who used WF_6 to deposit tungsten. This process also consumes the silicon substrate, however.

We have prepared the organometallic precursors $HCo(CO)_4$ and $SiH_3Co(CO)_4$ (eq. 1) by adapting the published syntheses [8] and used them to deposit cobalt and cobalt monosilicide, CoSi, respectively on the pore walls of both n- and p-type porous silicon. The rhenium analogue $HRe(CO)_5$ was prepared and used in an analogous way.

$$RX + NaCo(CO)_4 \rightarrow RCo(CO)_4 + NaX \qquad (1)$$

$(R = H \text{ or } SiH_3;\ X = Cl \text{ or } I)$

Preliminary conventional CVD experiments using dicobalt octacarbonyl, $Co_2(CO)_8$, as a precursor with argon carrier-gas quickly revealed that the cobalt films deposited on the porous silicon blocked the pores at the top surface and hence metal penetration down inside the pores was not observed. We therefore used more volatile, polar precursors such as $HCo(CO)_4$, $SiH_3Co(CO)_4$ and $HRe(CO)_5$, adsorbed these on to the pore walls of porous silicon in a static vacuum, and subsequently pyrolysed them in a two-stage process, using a dynamic vacuum in the second step. In this way, Co, CoSi and Re films were deposited on the internal pore walls, often down to the bottom of the pores. In a typical experiment, an n- or p-type sample of porous silicon with a pore size distribution between 40 and 80 Å, a porous density of approximately 65%, and a porous layer thickness of 2.5 μm was etched in 40% HF to remove native SiO_2 and placed in a horizontal, cold-walled reactor. The reactor was evacuated for about 3 h, and the sample then exposed for 3 min to the vapour from $HCo(CO)_4$ held at −35°C (vapour pressure = 1.3 mbar *) in a static vacuum. The porous sample was then heated to 100°C for 10 min before re-evacuating the reactor to remove any volatiles. After heating the sample for a further 10 min at 300°C in a dynamic vacuum, the wafer was allowed to cool to room temperature, before removing it from the reactor.

* 1 mbar = 100 Pa.

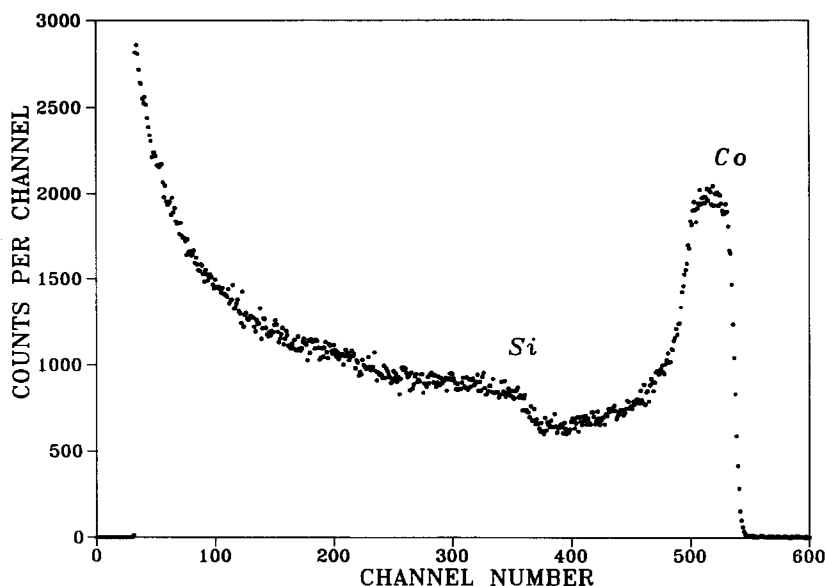

Fig. 1.

Analysis by Rutherford Back Scattering (RBS) [9] of a typical sample metallised with $HCo(CO)_4$ showed the presence of a 1000 Å surface layer which contained cobalt. Beneath this, the porous material contained both cobalt and silicon atoms in the ratio 1:1 (Fig. 1). At a level of 1.7 μm, the ratio was 1:5 (*i.e.* 17 atom% Co); this ratio remained constant down through the remainder of the porous layer (2.5 μm). Oxygen levels measured by (d,p) NRA [9] light element analysis were high: 25 atom% at the surface dropping to 20 atom% at the bottom of the porous layer. Carbon levels fell from 9 atom% down to 2% over the same distance (Fig. 2). These carbon levels are almost the same as those in un-metallised PS control samples, whilst oxygen levels are typically doubled. The increased levels of oxygen could be due, at least in part, to periods of atmospheric exposure before analysis of the metallised samples.

RBS analysis of a porous sample metallised for 3 min with vapour of the prevenient [6b] precursor $SiH_3Co(CO)_4$ held at −30°C (vapour pressure = 1.3 mbar*), using a similar two-step deposition process with temperatures of 150 and 450°C, showed that cobalt monosilicide was deposited (Fig. 3). In a typical run, a 1000 Å surface layer was deposited containing 25 atom% of cobalt and an equivalent amount of silicon. The carbon and oxygen levels were also each approximately 25 atom% in this region. Beneath the surface layer, the cobalt concentration ranged from 10 to 8% at a depth of 2 μm. Carbon levels decreased to 5 atom% below the surface layer, remaining constant down to 2 μm, whilst oxygen levels increased slightly to 30% over the same distance (Fig. 4). HRSEM studies and a preliminary EXAFS experiment gave evidence for metal silicide penetration into the pores and formation of CoSi respectively.

Secondary Ion Mass Spectroscopy (SIMS) has been used [10] to show the extent of uptake of molecular oxygen and hydrocarbons by PS on exposure to the atmosphere. There was evidence in our work that depositing a capping layer of

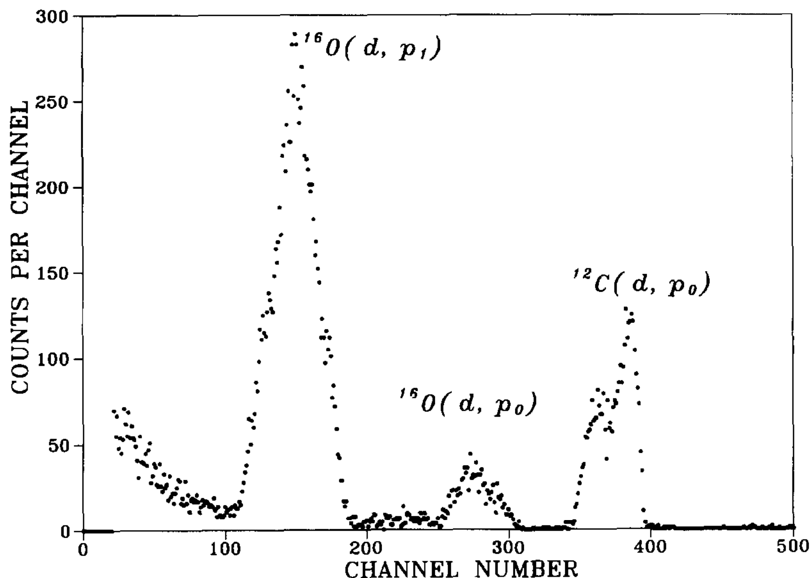

Fig. 2.

cobalt from $Co_2(CO)_8$ immediately after a deposition run involving $HCo(CO)_4$ or $SiH_3Co(CO)_4$ helped to limit the increased levels of oxygen and hydrocarbons normally observed.

In conclusion, we have shown that Co, CoSi and Re can be deposited on the internal surfaces of porous silicon by MOCVD. These films also contain substan-

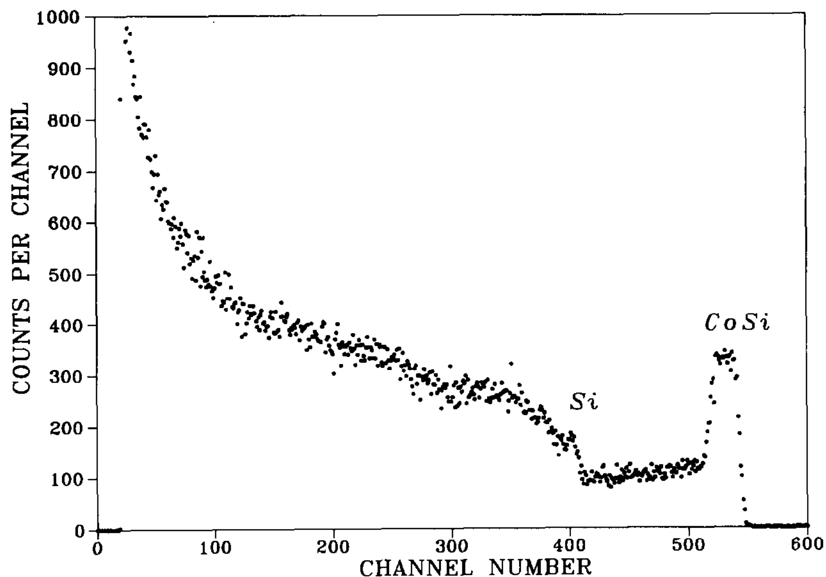

Fig. 3.

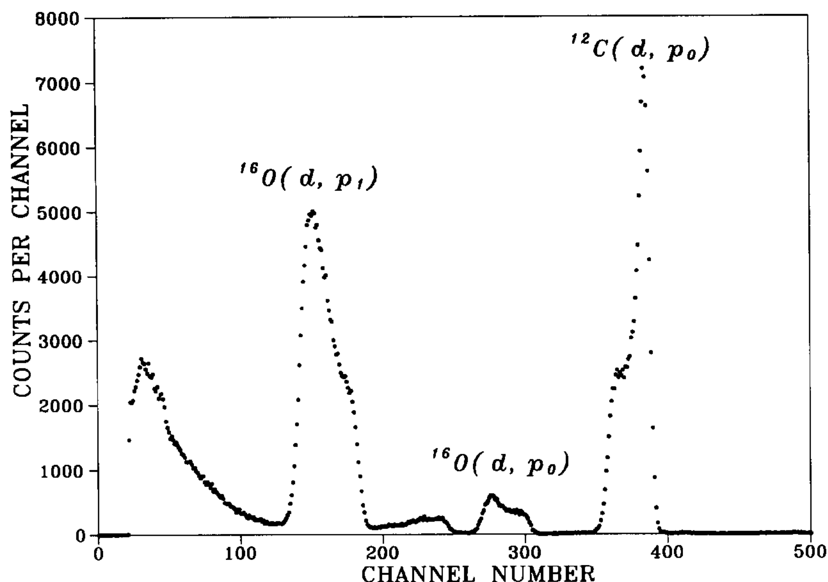

Fig. 4.

tial amounts of carbon and oxygen, although almost all of the carbon and some of the oxygen appear to be present in the porous region before deposition.

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