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Nickel thin films prepared by chemical vapour deposition from nickel acetylacetonate

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Nickel thin films were prepared by a low-temperature atmospheric-pressure chemical vapour deposition method. The raw material was nickel acetylacetonate. At a reaction temperature above 250 °C, polycrystalline nickel films can be obtained by hydrogen reduction of the raw material. The resistivity (8.1–13.3 μΩ cm) of the film was close to that of bulk nickel.

1. Introduction

Nickel films are widely used in the metallization of ferrites and as decorative and corrosion-resistant coatings, and as selective absorbers in solar thermal energy conversion. Nickel is also a promising material for microelectronics because the electrical resistivity is low and the oxidation resistance is high.

Recently, chemical vapour deposition of nickel has attracted much attention for obtaining smooth adherent films of low resistivity. Various chemical vapour deposition methods [1–6] have been proposed: for example, the decomposition of nickel tetracarbonyl [1–4] at 250–300 °C, the hydrogen reduction of nickel hexafluoroacetylacetonate [5] at 250 °C, or the hydrogen reduction of dimethylnickel [6] at 200 °C.

In this paper, nickel acetylacetonate is proposed as a source material in the low-temperature atmospheric-pressure chemical vapour deposition method. The nickel films were deposited by hydrogen reduction of nickel acetylacetonate at a temperature above 250 °C.

2. Experimental procedure

Nickel acetylacetonate of reagent grade was used as the source material. It is a solid at room temperature. Fig. 1 shows a schematic representation of the experimental set-up. Nickel acetylacetonate was heated at a temperature of 200–220 °C and the generated gas was entrained by nitrogen carrier gas. The flow rate of the carrier gas was 300 cm^3 min^{-1}. Hydrogen gas was injected into the nozzle and mixed with the source gas. The flow rate of H_2 gas ranged from 300 to 1000 $cm^3 min^{-1}$.

A 76 mm × 26 mm borosilicate glass plate was used as the substrate. The substrate was placed in the closed-tube reactor heated by an external electric furnace. The reaction temperature was in a range 250–350 °C. The total pressure in the reactor was equal to atmospheric pressure.

The morphology of the film was measured by a scanning electron microscope. The crystallinity of the film was analysed by the X-ray diffraction method with CuK_α radiation. The electric resistivity of the film was measured by the van der Pauw method.

3. Results and discussion

Nickel films were grown by the hydrogen reduction of nickel acetylacetonate. In an inert (nitrogen) atmosphere, no nickel film was obtained. At a reaction temperature above 250 °C, smooth nickel films were formed on the borosilicate glass substrates. The films were highly adherent and showed no apparent peeling from the glass substrates.

The colour and surface morphology of the film changed with the film thickness. When the film thickness was less than ~50 nm, the film was translucent although the surface was a shiny mirror. It was not until the thickness was increased above ~50 nm that the film was electrically conductive and adherent on the glass substrates. When the thickness was increased further above ~200 nm, the surface became dull and pale nickel in appearance.

Fig. 2 shows plane-view scanning electron micrographs. The nickel films were obtained at a reaction temperature of 270 °C. The surface pattern is seen to be rather flat in 55 nm thick film, and it is stereoscopic in 184 nm thick film. A comparison of Fig. 2a–c suggests that preferred overgrowths occur on the nickel film of thickness ~100 nm, making a vertically developing three-dimensional rough and coarse structure, several hundred nanometers in height. Thus, the surface becomes dull and pale nickel in appearance when the thickness of the film is over ~200 nm.

Fig. 3 shows the Arrhenius plot of deposition rates, obtained at a source temperature of 220 °C and H_2 flow rate of 0.3 $cm^3 min^{-1}$. The deposition rate increases with increasing reaction temperature from 250 to 270 °C. It saturates at a temperature of 270 °C and even decreases with temperature above 270 °C. This temperature is close to the thermal decomposition temperature of nickel acetylacetonate, which is reported to be 300 °C. Therefore, the decrease in deposition rate seems to be associated with the thermal decomposition of nickel acetylacetonate. Thus nickel acetylacetonate available for hydrogen reduction decreases in concentration with increasing reaction temperature above 300 °C, through thermal decomposition in the vapour phase.

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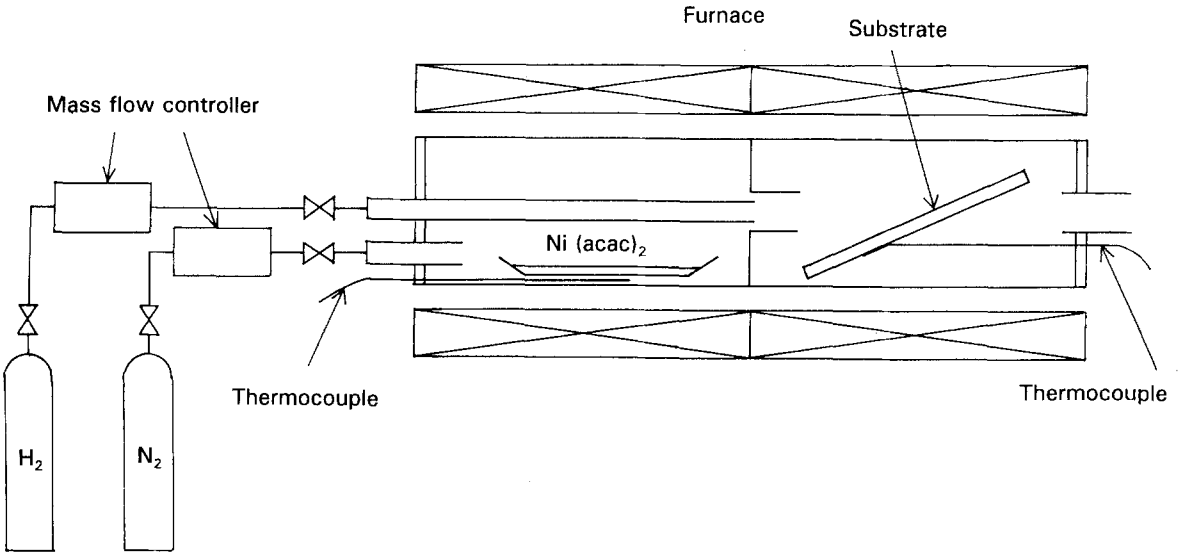
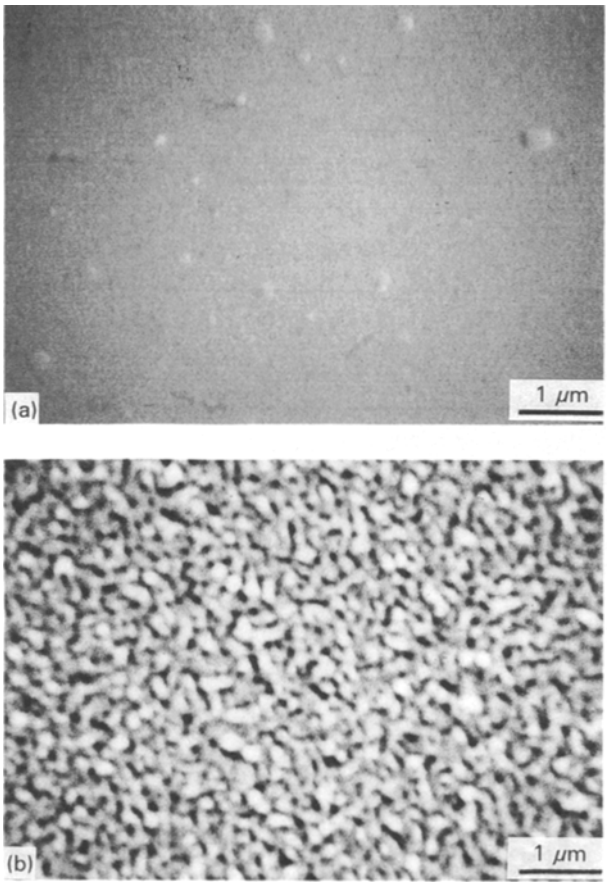


Figure 1 Schematic representation of experimental equipment.



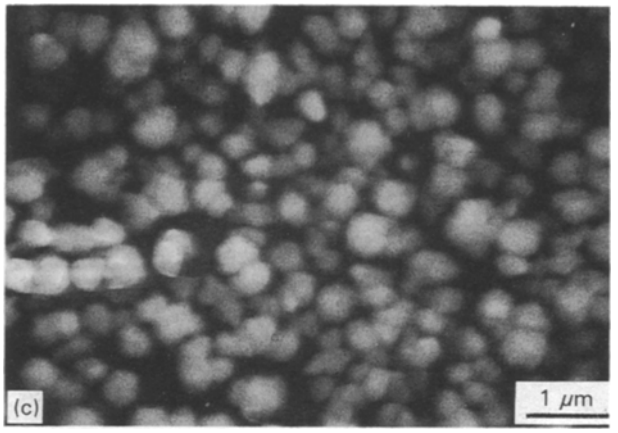


Figure 2 Plane-view scanning electron micrograph of nickel films of thickness (a) 55 nm, (b) 124 nm and (c) 184 nm.

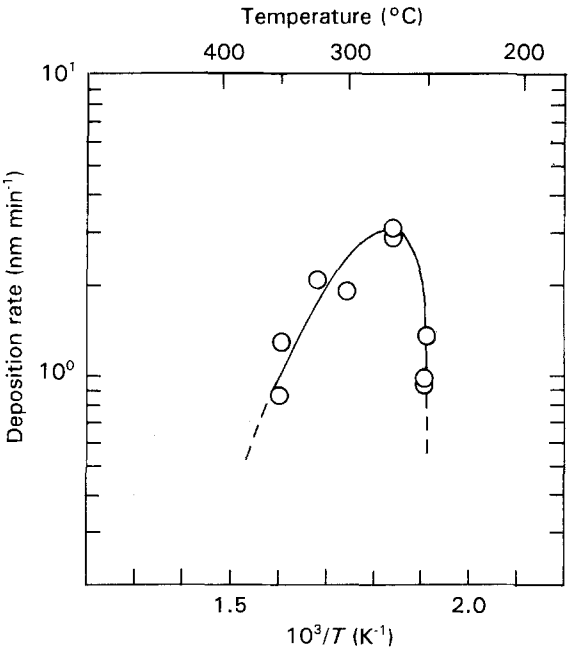


Figure 3 Arrhenius plot of deposition rate of nickel film.

Fig. 4 shows typical examples of X-ray diffraction patterns of the nickel film. The X-ray diffraction patterns showed that the nickel film was composed of crystallites with a predominantly cubic structure. The films obtained at a reaction temperature below 270 °C show prominent peaks of the (1 1 1) plane, which is a natural growth plane for a face-centred cubic metal like nickel. A slight deviation from this [1 1 1] preferential orientation for the films deposited at reaction temperatures above 300 °C may be at-

tributable to an effect of the thermal decomposition of nickel acetylacetonate in the vapour phase.

The resistivity of the nickel film depended only on film thickness, being independent of the deposition temperature. Fig. 5 shows the resistivity of nickel film as a function of film thickness. The resistivity ranged from 8.1 to 13.3 μΩ cm, showing the lower values in a range of film thickness 60–150 nm. It is noted that the lowest value is very close to that for bulk nickel (6.8–7.5 μΩ cm). There is a weak dependence on film thickness, the resistivity having relatively higher values at both lower (~50 nm) and higher (~200 nm) values of film thickness. The higher resistivity at film thickness ~50 nm is attributable to surface effects, and the higher resistivity at ~200 nm is attributable to the surface morphology of the film, as follows. While the ~ 100 nm thick film has a smooth surface, the 200 nm thick film has a rough surface region (see Fig. 2) which is less conductive for electricity than the smooth surface.

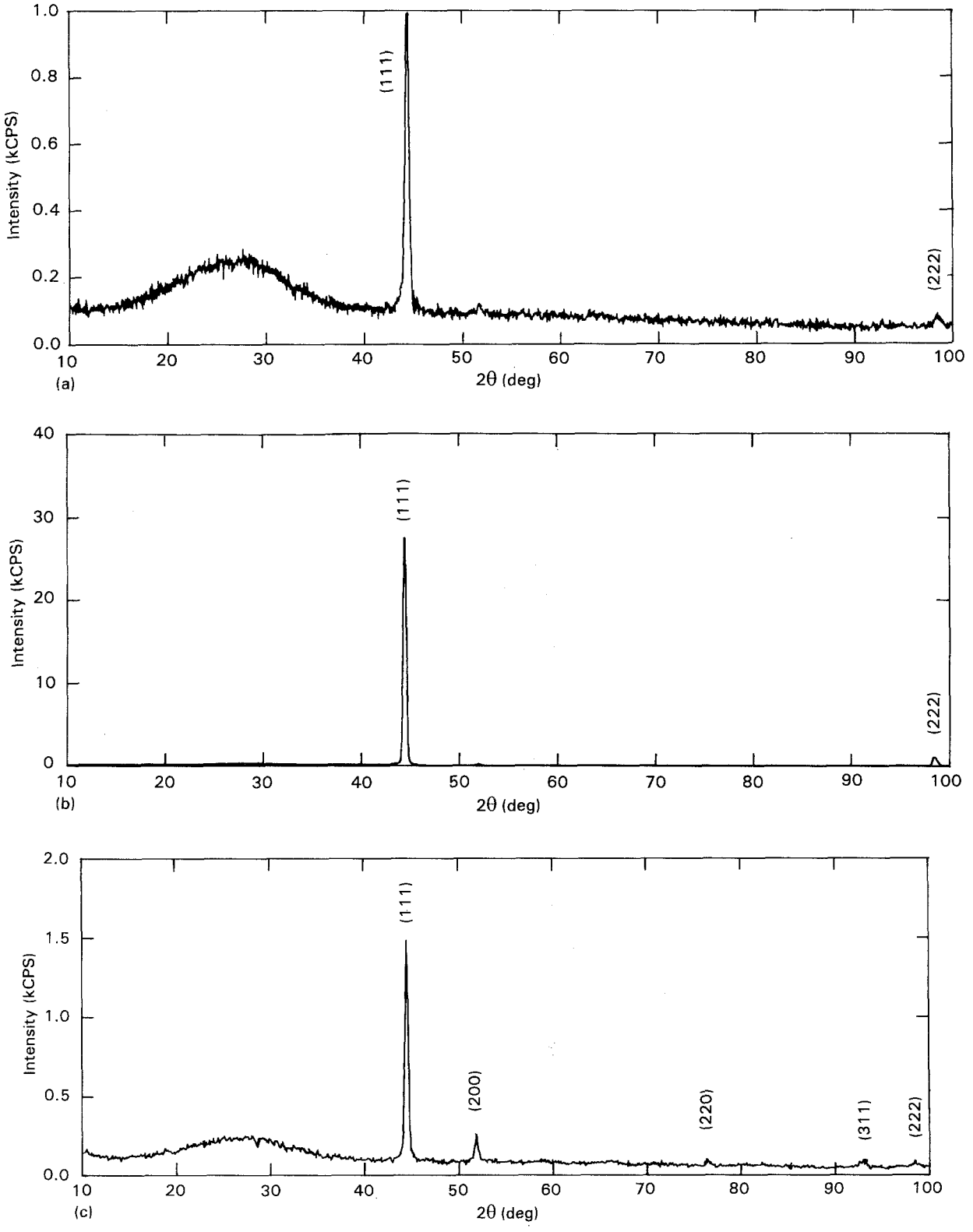


Figure 4 X-ray diffraction patterns of nickel films obtained at different reaction temperatures: (a) 250 °C, film thickness 56 nm; (b) 270 °C, 184 nm; (c) 300 °C, 116 nm; (d) 350 °C, 78 nm.

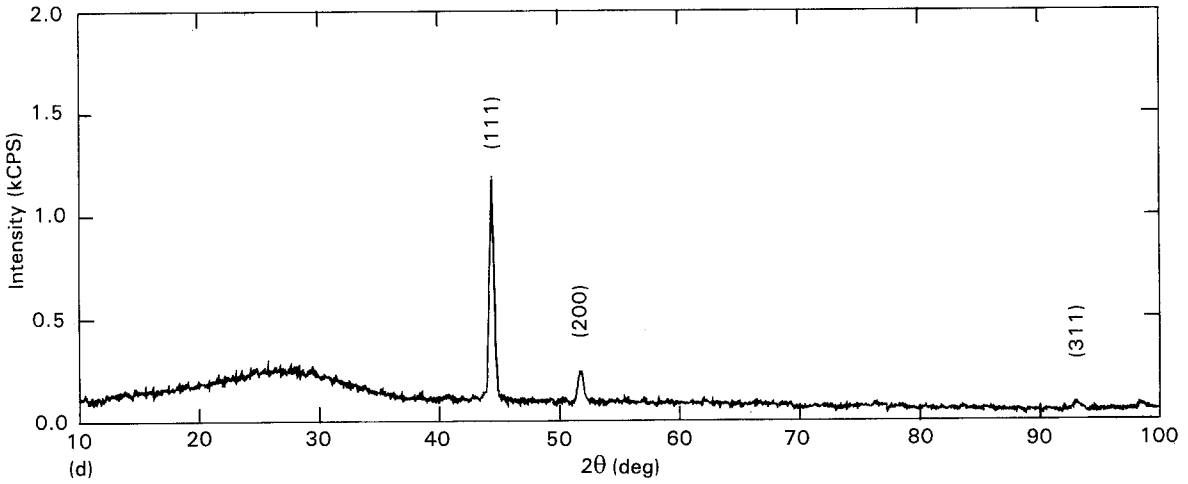


Fig. 4 continued

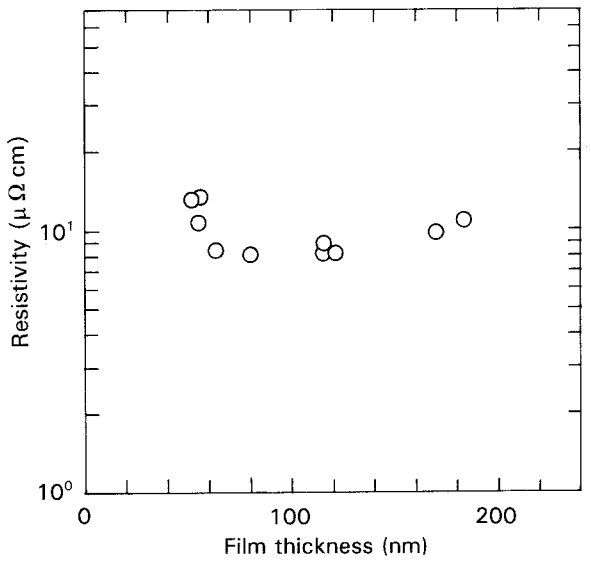


Figure 5 Resistivity of nickel film as a function of film thickness.

4. Conclusion

Nickel thin films were prepared by a low-temperature atmospheric-pressure chemical vapour deposition method. The raw material was nickel acetylacetonate. At a reaction temperature above 250 °C, polycrystalline nickel films can be obtained by hydrogen reduction of the raw material. The resistivity (8.1–13.3 μΩ cm) of the film was close to that of bulk nickel.

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