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Sputter Epitaxy of Ag and Ni Films[2])

By

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Epitaxial films of silver are grown by sputtering on mica substrates at elevated temperature. A systematic study of samples grown on different substrates and at different temperatures is carried out using X-ray diffraction ($\theta-2\theta$ and Laue). Both the temperature and substrate play crucial roles for the growth of epitaxial films. The growth of epitaxial Ni on Ag single crystal by sputtering is also reported.

Epitaktische Schichten von Silber auf einer Glimmerunterlage werden mit der Sputtertechnik bei erhöhten Temperaturen hergestellt. Proben, gezogen bei verschiedenen Temperaturen und auf verschiedenen Substraten, werden systematisch mit Röntgenstreuung ($\theta - 2\theta$ und Laue) untersucht. Sowohl Temperatur wie Substrat sind entscheidend beim epitaktischen Wachstum der Schichten. Im weiteren wird über durch Sputtern gewonnene epitaktische Ni-Schichten auf Ag-Einkristallen berichtet.

1. Introduction

The epitaxy of Ni on Ag as well as Ag on Ni by *evaporation* has already been reported [1 to 4]. Since Ag is known to be insoluble in Ni, this combination of materials is a likely candidate for the preparation of layered metallic superstructures. Unlike evaporation, sputtering allows control over the energy distribution of the particles incident on the substrate which, in principle, can be a unique advantage for the preparation of superstructures. However, to our knowledge, there have been no previous reports of epitaxy of Ag on Ni by sputtering. The present work reports the preparation of sputtered epitaxial single crystal Ag and Ni films at elevated temperatures.

2. Sample Preparations

Samples were prepared using a sputtering system which consists of two high rate dc magnetron sputtering guns [5]. The two guns are located ≈ 38 cm from each other and shielded, so no overlap of the two beams is detectable (Fig. 1). The substrates are held on a heated rotating table which can move the substrate from one beam to the other. For the work reported here, the substrate distance above the source was held constant at 11.5 cm. Quartz lamps and a rotating contact thermocouple were used to control the temperature of the substrate in the range room temperature to 400 °C. Six nines purity argon gas was used for the sputtering.

Sputtering has several advantages over vacuum evaporation. During sputtering, the source to substrate distance and sputtering gas pressure can be separately arranged so that the sputtered atoms thermalize to the temperature of the argon sputtering gas [6]. For refractory metals this leads to an energy distribution much narrower

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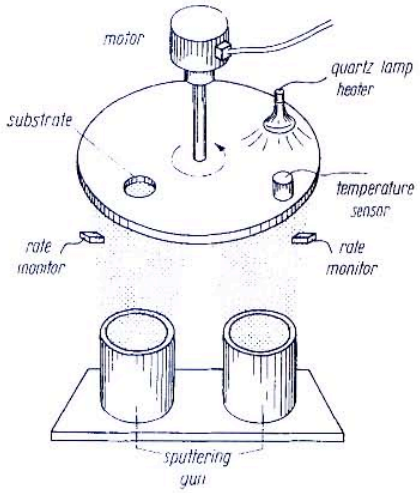

Fig. 1. Schematic of sputtering system

than that obtained by evaporation [6].

The sputtered films for this work were produced at 10 mTorr of Ar pressure as measured both by a capacitance pressure transducer and also by a conventional wide range ionization gauge. Target current densities were in the range 10 to 100 mA/cm² at voltages of 100 to 800 V. Prior to deposition of each set of samples the system was pumped to $\approx 3 \times 10^{-7}$ Torr. A throttling valve was then inserted above the diffusion pump and Ar gas admitted through a needle valve to maintain a dynamic equilibrium sputtering gas pressure. After introduction of the Ar gas the sputtering rate was controlled by keeping pressure and power constant. Sputtering rate for the present work was set at 35 Å/s.

The samples were prepared on muscovite mica, sapphire (90° orientation), and crystalline MgO substrates. For cleaning, the mica was freshly cleaved whereas sap-

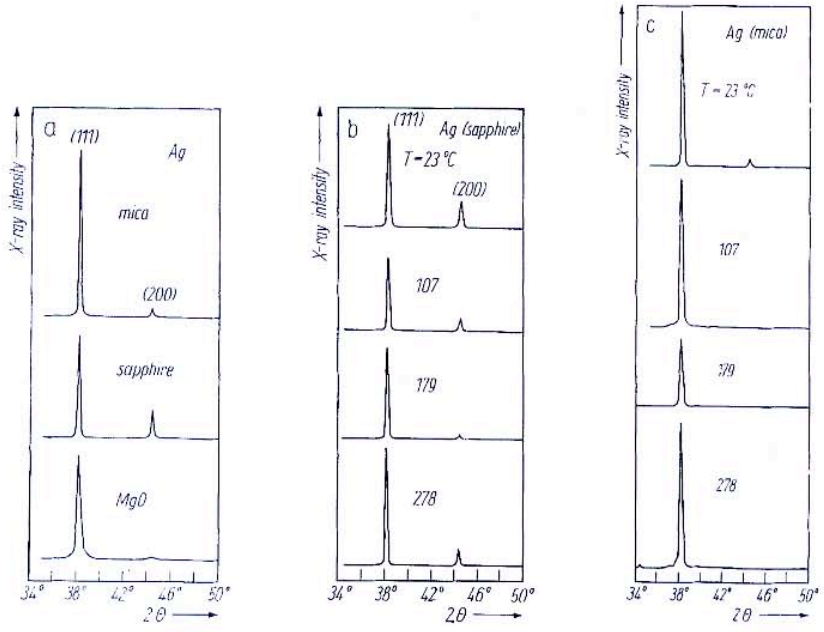

Fig. 2. Bragg diffraction scans for Ag grown a) on mica, sapphire, and MgO at 23 °C; b) on sapphire at four different temperatures; and c) on mica at four diffèrent temperatures

phire and MgO were cleaned by detergent, distilled water and finally by ethyl alcohol using an ultrasonic cleaner.

3. Silver

Ag samples were prepared as described above and were X-rayed using CuK_α radiation. The θ–2θ scans for samples grown at room temperature are shown in Fig. 2a. It can be seen that for all three substrates, the (111) peak is much stronger than the (200) peak indicating preferential (111) orientation perpendicular to the substrate. Of the three substrates, the ratio of intensity of (111) to (200) is higher on MgO than on mica or sapphire. However, the (111) peak is narrower on the mica and sapphire compared to MgO indicating a better texture. Fig. 2b shows the θ–2θ plots for samples grown on 90° oriented sapphire at 23, 107, 179, and 278 °C. The (200) peak remains for all temperatures. Laue X-ray diffraction (not shown here) showed rings characteristic of a polycrystalline sample for all of these samples. θ–2θ plots for samples grown on mica at elevated temperatures are shown in Fig. 2c, and Laue photographs of samples removed from the mica are shown in Fig. 3. The sample grown at 107 °C shows only (111) ordering along the Z direction with no detectable (200) line to within better than one part in 300. However, the Laue of the same sample shows rings indicating polycrystallinity in the x–y plane. For the sample grown at 179 °C, the Laue shows both polycrystalline rings and single crystal spots indicating that there is some

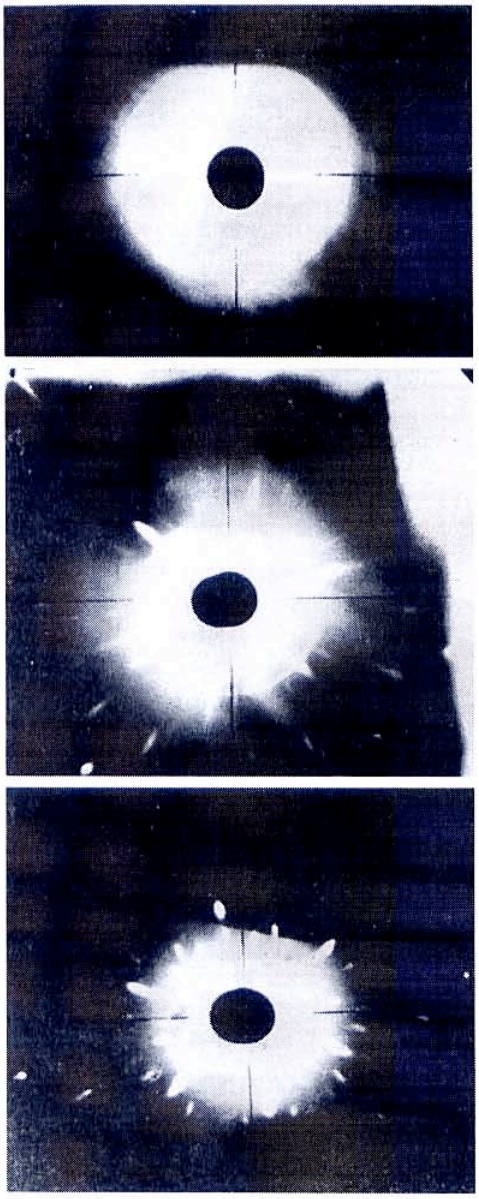

Fig. 3. Laue photographs of Ag on mica at a) $T = 23$, b) 179, and c) 278 °C

ordering in x–y plane. The sample grown at 278 °C shows no evidence for a (200) peak on the θ–2θ diffraction and only spots in the Laue indicating epitaxial growth of Ag by our sputtering process. The six spots (rather than three as expected from the three-fold symmetry of the (111) plane) indicates twinning of the Ag. This is discussed in more detail below.

4. Nickel

The θ–2θ diffraction results for nickel samples grown on mica, sapphire, and MgO at room temperature are shown in Fig. 4a. The diffraction results for nickel samples grown at elevated temperatures are shown in Fig. 4b. In all cases the (200) peak continued to appear in the X-ray diffraction curves along with the (111) peak. Also Laue diffraction from these samples (not shown in paper) showed only polycrystalline rings.

Nickel was also grown on freshly prepared single crystal Ag substrates. Prior to deposition of the Ni, 0.2 μm thick films of (111) oriented Ag were grown on mica at approximately 275 °C using the procedure described above. Immediately following this deposition the substrate temperature was restabilized at a new value (maximum time 1 h) and approximately 1 μm thick Ni films grown. Fig. 4c shows the θ–2θ diffraction result for room temperature Ni on Ag substrates where we can see (111) peaks of Ag and Ni as well as a weak (200) peak of Ni. Laue diffraction from this sample shows polycrystalline rings from the Ni (Fig. 5): the single crystal spots expected from the epitaxial Ag layer are too low in intensity to show on this photograph. Fig. 4c and 5 also show θ–2θ and Laue diffraction results for an Ag–Ni sample grown at 275 °C where we observe strong (111) peaks of Ag and Ni with no trace of (200) peaks. Also the Laue diffraction from this sample shows only spots demonstrating epitaxy of the Ni film grown on the freshly prepared Ag substrate (on mica) at 275 °C.

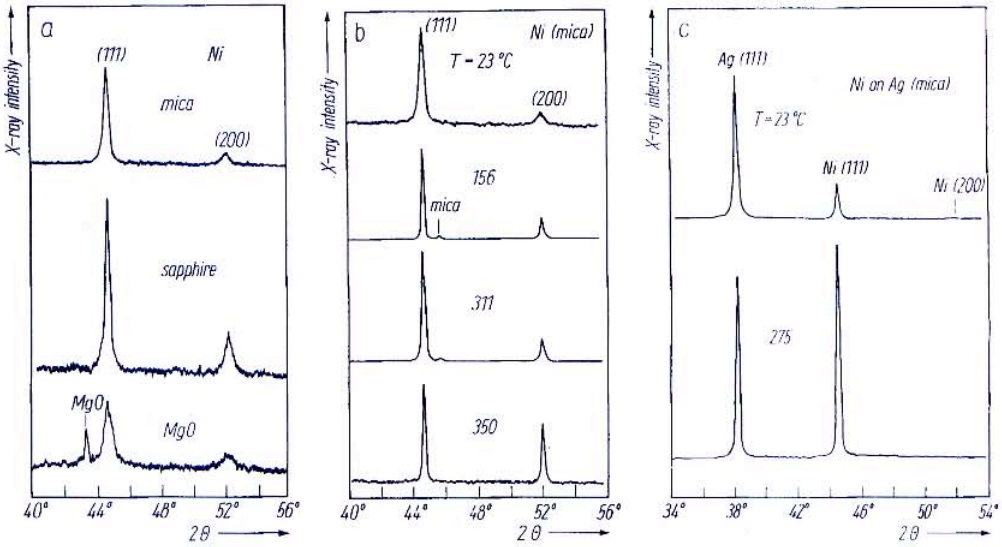

Fig. 4. Bragg diffraction scans for Ni a) on mica, sapphire, and MgO at 23 °C; b) on mica at four different temperatures; and c) on Ag samples grown on mica substrates at T = 23 and at 275 °C

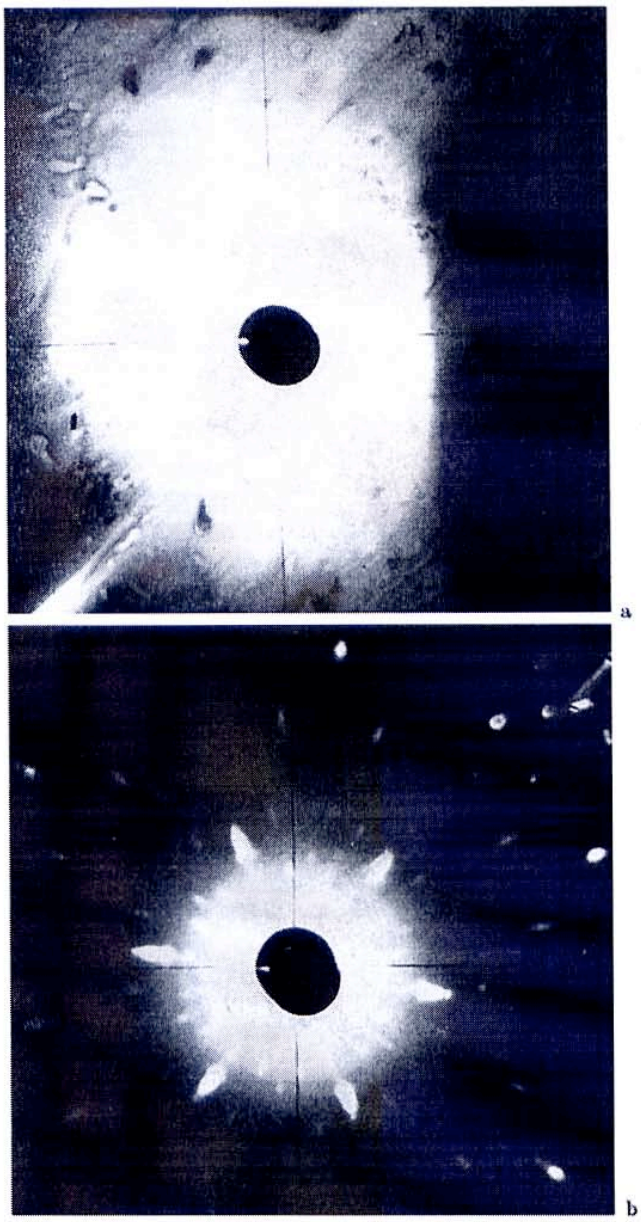

Fig. 5. Laue photographs of Ni and Ag samples grown on mica substrates at a) $T = 23$ and at b) 275 °C

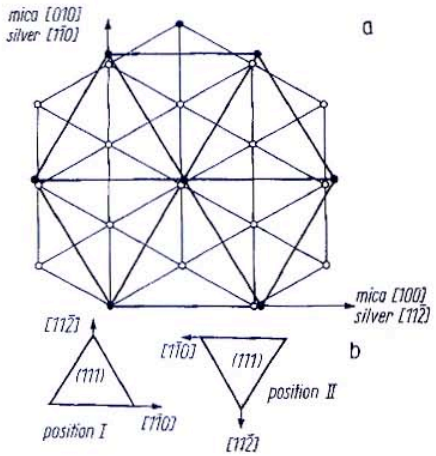

Fig. 6. a) The fit of the main silver orientation on mica (after Pashley); ● potassium ion sites in mica (001), ○ silver atoms in (111) plane. b) Views of the two (111) silver orientations on mica (after Dickson and Pashley)

5. Discussion

Pashley and Dickson [7, 8] have observed that when silver is deposited by vacuum evaporation onto cleaved surfaces of heated mica, it is oriented with (111) Ag parallel to (001) mica and with [1$\bar{1}$0] Ag parallel to [010] mica. A second orientation can also occur, namely (111) Ag parallel to (001) mica with [$\bar{1}$10] Ag parallel to [010] mica. The two orientations are equivalent as regards the atomic fitting between the contact planes of mica and silver. The relation between the two orientations is that of twins on the (111) plane (Fig. 6) since a rotation of 180° about [111] changes position I to position II. This explains why, instead of three-fold symmetry, we see six-fold symmetry spots in the Laue of Ag films on mica (Fig. 3). Reichelt [9] has also reported six-fold symmetry Laue spots of vacuum evaporated Ag film on mica indicating twinning as has Matthews [10].

Gonzalez [11] has studied evaporated epitaxial Ni on Ag and has observed that Ni always grows with (111) planes parallel to the (111) plane of silver, and in two twin-related orientations in which [$\bar{1}$10] Ni is parallel to [1$\bar{1}$0] Ag and [1$\bar{1}$0] Ni parallel to [1$\bar{1}$0] Ag. The same orientation has been observed by other workers [12]. Also using evaporated samples, Shirai et al. [4] have observed the orienatations as (001) Ni parallel to (001) Ag and (100) Ni parallel to (100) Ag.

We should note that Chopra and Randlett [13] have reported sputtered epitaxy of Ag film at liquid nitrogen temperature (77 K). However, our samples are grown at elevated temperatures, and their growth patterns are different from ours.

While epitaxial Ni film has been grown [9] before by vacuum evaporation on mica, in the present work using the growth parameters described above we were unable by sputtering to grow epitaxial Ni films on mica at temperatures as high as 350 °C.

6. Concluding Remarks

We report for the first time, the sputtered epitaxy of Ag on mica substrates at elevated temperature (278 °C) and Ni on (111) Ag single crystal substrates at 275 °C. Other substrates, namely sapphire and MgO were also tried but with no success. Ni could not be grown expitaxially on mica at room temperature or at elevated temperatures up to 300 °C or at various pressures in the range 5 to 20 mTorr.

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