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STRUCTURE AND PROPERTIES OF THE NANOSTRUCTURED Al-Si ALLOYS

B. B. STRAUMAL[1, 2, 6], N. F. VERSHININ[1], V. N. KURLOV[1, 2], V. SURSAEVA[2], S. PROTASOVA[2], N. E. SLUCHANKO[3], T. V. ISHENKO[3,6] , S. TISHIN[5], P. ZIEBA[4, 6], W. GUST [6]

([1]I. V. T. Ltd., P.O. Box 47, RU-109180 Moscow, Russia; [2]Institute of Solid State Physics, Chernogolovka, 142432 Moscow District, Russia; [3]General Physics Institute, 117942 Moscow, Russia; [4]Institute of Metallurgy and Materials Science, 30059 Cracow, Poland; [5]Institute of Electronics of Uzbek Academy of Sciences, 700143 Tashkent, Uzbekistan; [6]Institut für Metallkunde, 70174 Stuttgart, Germany)

The kinetics of phase separation after the quenching of a binary alloy system into the miscibility gap is the problem of great interest. One of the most convenient objects to study this class of phenomena are the non-equilibrium substitutional solid solutions formed from metal and semiconductor elements such as Al_{1-x}–Si_x. They can be obtained for example under high pressure treatment or various deposition methods. In this work the thin films of the Al_{1-x}–Si_x alloys were obtained with the aid of magnetron sputter deposition method in form of thin films on the oriented single crystalline sapphire substrates. The microstructure of the films was studied with the aid of analytical electron microscopy. The data on the resistivity measurements permitted to compare the properties of magnetron deposited solid solutions with those of supersaturated solid solutions obtained under high pressure.

INTRODUCTION

The kinetics of phase separation after the quenching of a binary alloy system into the miscibility gap is the problem of great theoretical and practical interest [1-3]. The dominant processes observed are the demixing of the homogeneous system into single-phase regions and the consequent increase in the average size of these regions, known as coarsening. One of the most convenient objects to study this class of phenomena are non-equilibrium substitutional solid solutions formed from metal and semiconductor elements such as Al_{1-x}–Si_x and Al_{1-x}–Ge_x. They can be obtained for example under high pressure treatment or [4, 5]. In the Al–Si and Al–Ge systems the solubility of Si and Ge in Al by increasing pressure drastically increases [4-6]. In the case of $Al_{1-x}Si_x$ solid solutions the solubility limit is beyond 15 at. % Si at 5.4 GPa [4] in comparison with 1.59 at. % Si at the atmospheric pressure. The application of high pressures up to 10 GPa and rapid quenching to liquid nitrogen temperatures has allowed the authors of [6] to elevate the solubility limit up to $x = 0.2$ for Al_{1-x}–Si_x. Additional interest to the Al–Si solid solutions is caused by the strong enhancement of the superconductivity in the vicinity of the lattice instability limit [7]. The phase separation process and suppression of superconductivity are closely related to each other in these materials. Moreover, an essential enhancement of the electron-phonon interactions has been found [7, 8] in the metastable Al_{1-x}–Si_x solid solutions, which can be attributed to the appearance of the so-called "cluster phonon

modes". Therefore, a comprehensive investigation of non-equilibrium state in Al_{1-x}–Si_x appears as very attractive and prominent to clarify both the features of decay kinetics and the origin of the superconductivity enhancement in the vicinity of lattice instability in Al.

The methods of deposition of the thin films are very attractive to produce the samples with various structure and properties. Especially interesting is the possibility to produce in one experiment the samples with various concentrations creating and controlling the conditions for lateral or depth gradient [9, 10]. The non-equilibrium conditions during the deposition allows one to produce the stable and metastable phases in the films [11, 12]. Therefore, the goal of this work was to study the possibility to produce the range of the metastable Al-Si alloys with the aid of magnetron sputter deposition.

EXPERIMENTAL OUTLINE

The deposition apparatus used in this work consists of vacuum chamber having the form of a horizontal cylinder of 700 mm diameter and 700 mm length. Its pumping system consists of a Balzers turbomolecular pump with a capacity of 1500 *l* /s and two rotary pumps with a total capacity of 40 *l* /s. A total pressure of 6×10^{-5} Pa may be achieved without deposition process. The apparatus can be used both for magnetron sputter deposition and for vacuum arc deposition [13]. On opposite ends of the vacuum chamber deposition the sources are placed. This configuration allowed to get the concentration gradient along the axis of the chamber exploiting two cathodes with different metals [9].

In this work the twin cathode was manufactured. The cylindrical cathode having the diameter D = 60 mm contained two semi-cylinders made of pure 99.999% Al and Al containing about 10 at. % Si (semiconductor purity). The contact line of both half-cylinders was vertically oriented (Figure 1). The substrates to be coated were positioned on the horizontal holder along a straight line parallel to the cathode surface and perpendicular to the border between Al and Al-Si cathode halves (Fig. 1). The sample 1 was close to the Al half, the sample 6 was close to the Al-Si half. The substrates with diameter of 20 mm and thickness 0.5 mm were made from polished sapphire single crystals [14]. Another set of samples was made of fresh cleaved NaCl single crystals. After deposition of Al-Si thin films, the samples on the sapphire substrates were quenched into the liquid nitrogen and were kept at 77 K until the resistivity

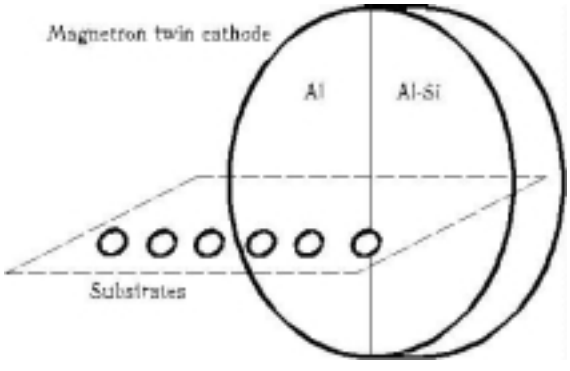

Fig. 1. Scheme of the magnetron sputter deposition of the Al-Si alloys from the twin cathode.

measurements. The concentration of Si in the samples was controlled with the aid of electron probe microanalysis (EPMA).

The observation of the microstructure was carried out using a transmission electron microscope (TEM) Philips CM 20 Twin operating at 200 kV and equipped with an energy dispersive X-ray spectrometer (EDX) Link exL, enabling a high spatial resolution analysis of local changes in the solute content. The microscope was operating at a 200 kV accelerating voltage in the nanoprobe mode with a LaB_6 source of electrons. The size of the incident electron beam was 3-9 nm in diameter at the »full width at half maximum" (FWHM). The specimens were tilted approximately 20 degrees towards a Si(Li) X-ray detector which resulted in a 40^o take-off angle. The average foil thickness calculated from the contamination spots at the top and bottom of the foil was 95-210 nm. The intensity of the characteristic X-ray peaks $I_{Al\text{-}Ka}$ and $I_{Si\text{-}Ka}$ were obtained for a X-ray acquisition time of 100 seconds.

To establish the kinetics of solid state transformation of the supersaturated $Al_{1-x}Si_x$ solid solutions the isothermal resistivity has been investigated in different Al–Si samples. In accordance with [15] the «metastable part» of resistivity $\Delta\rho$ of Al–Si alloys is connected with the Si-atoms concentration in fcc Al-rich matrix, and it is possible to analyze the features of decomposition process through the study of the resistivity relaxation behavior $\Delta\rho(T, t)$. The data for magnetron sputter deposited Al–Si films were compared with the »final" resistivity curves $\rho_\infty(t, T) = \lim_{t\to\infty} \rho(t, T)$ for the Al–Si alloys obtained by the high pressure treatment [16]. The $\rho_\infty(T)$ dependence was obtained by temperature measurements of the samples completely annealed at T^f = 620K and then $\rho_\infty(T)$ were used in our previous work to extract the non-equilibrium part of $\Delta\rho(t, T)$ [16].

RESULTS AND DISCUSSION

The values of Si content in 6 studied Al-Si thin films measured with the aid of EPMA are 0, 2.2, 4.1, 6.1, 8.0 and 9.5 at. %. For each sample the Si concentration does not fluctuate in the direction parallel to the vertical axis of the twin cathode during the deposition. Slight gradient on each sample can be seen in the perpendicular direction. Therefore, the used method of twin cathode really allows one to deposit coatings with lateral concentration gradient with the uniform concentration in the direction parallel to the vertical axis of the twin cathode. If the dimension of possible Si-particles is much lower than the diameter of analyzed area (about 1 μm), the EPMA data give the brutto-concentration and cannot allow to distinguish the solid solution and the alloy containing two phases.

The resistivity measurements for the same family of Al-Si alloys shows that the resistivity at 77 K for the all samples including pure Al is nearly the same (about 0.5 mOhm.cm). We can suppose that during the deposition and subsequent treatment the Al-Si alloy demixed and fine Si precipitates formed in the matrix. In this case the resistivity value in all samples is controlled by the depleted Al matrix with Si concentration equal to the solidus value. The same behaviour was observed for the

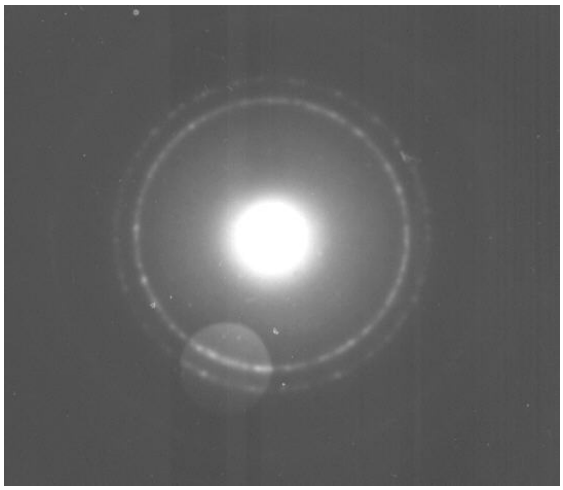

Fig. 2. Electron diffraction pattern for the magnetron sputter deposited Al-4.1 at. % Si thin film.

supersaturated Al–Si alloys produced by the high-pressure treatment after their demixion and phase separation.

This hypotesis has been proved with the aid of analytical TEM. The electron diffraction pattern (Fig. 2) shows that the film is crystalline and non-textured. The Si-rings are very weak and almost absent. The bright-field TEM picture (Fig. 3) shows that the Al-matrix contains very fine particles. The dark field TEM micrograph (Fig. 4) evidences that the mean diameter of these particles is about 5–10 nm. The Al grains are rather large (50 to 10 nm) in comparison with these particles.

Individual grains of Al-matrix can be seen in the bright field micrographs (Figs 5 and 6). The particles are randomly distributed in the bulk of Al grains. Some particles are localized at the grain boundaries forming the chains (Fig. 5). The microanalysis was performed in the field containing larger particles (Fig. 6). Points 1 to 3 were localized in the Al-matrix without visible particles. Point 4 was localized in the particle which is larger that the beam diameter. The Si content in points 1 to 3 is about 3 to 4 wt. %. Therefore, these points correspond to the Al-Si depleted solid solution. In the point 4 the Si content is about

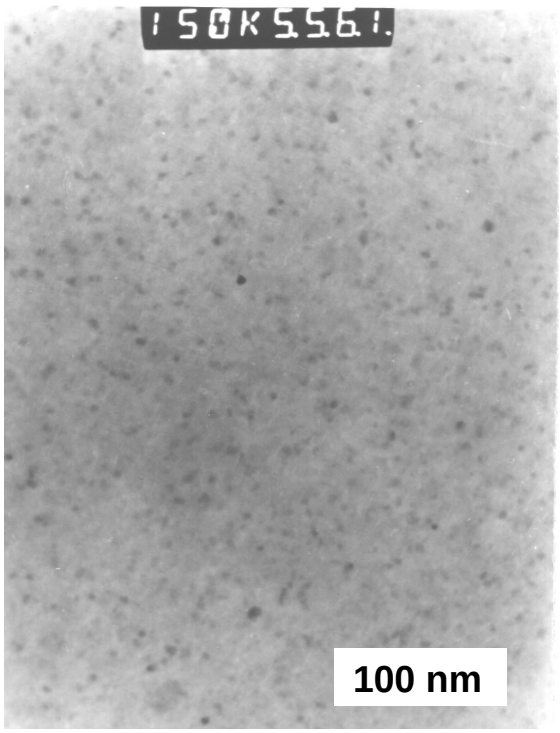

Fig. 3. TEM bright-field micrograph of the magnetron sputter deposited Al-4.1 at. % Si thin film showing fine Si particles.

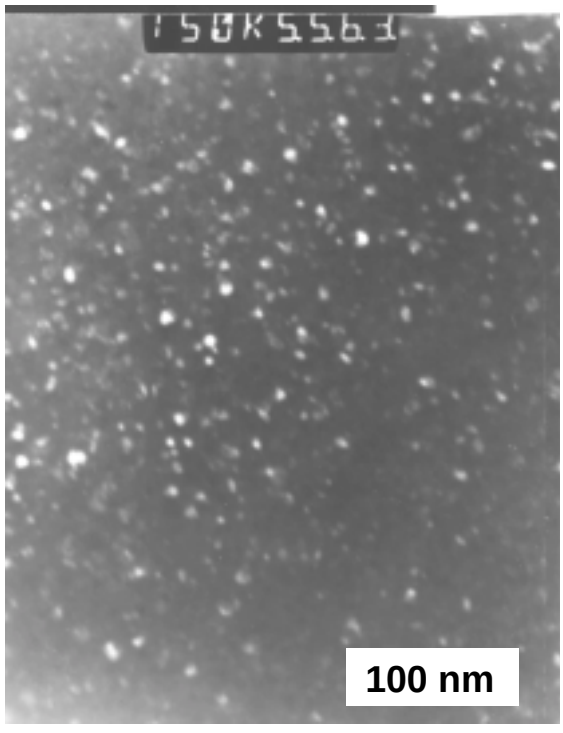

Fig. 4. TEM dark-field micrograph of the magnetron sputter deposited Al-4.1 at. % Si thin film showing fine Si particles.

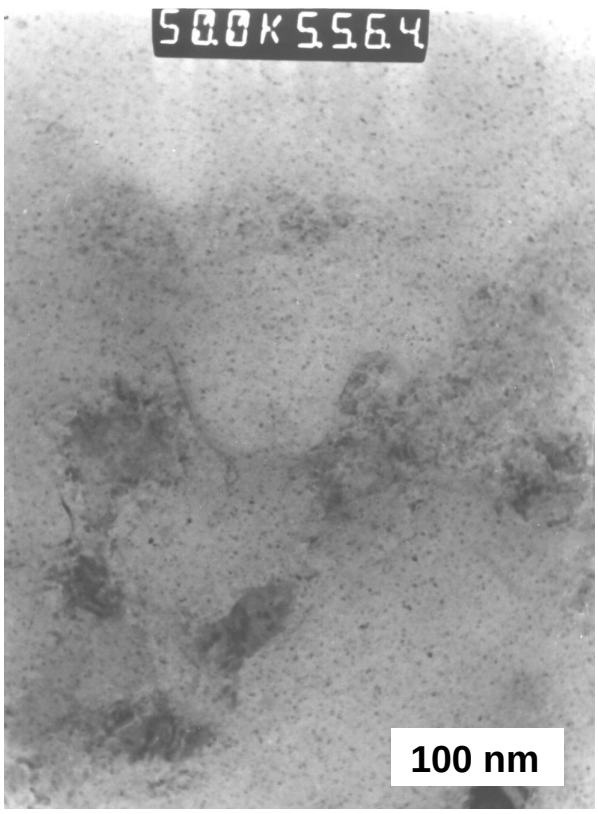

Fig. 5. TEM bright-field micrograph of the magnetron sputter deposited Al-4.1 at. % Si thin film showing grains in Al-matrix and fine Si particles in the bulk and along the grain boundaries.

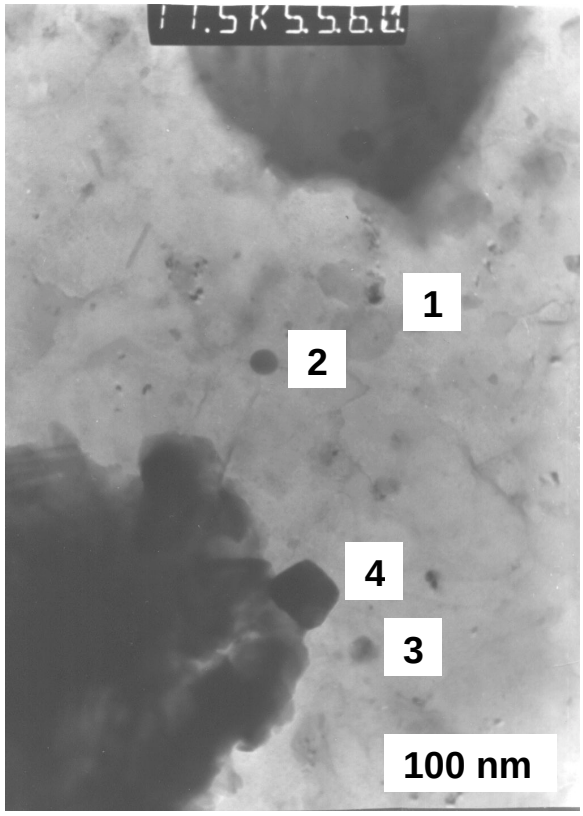

Fig. 6. TEM bright-field micrograph of the magnetron sputter deposited Al-4.1 at. % Si thin film showing depleted Al-matrix and Si particles in the bulk. The points of chemical analysis are marked by arrows.

43 wt. %. This value is lower than equilibrium solubility of Si in the Al-Si system. But the diameter of analyzed particle is lower that the sample thickness, and the concentration value is measured in the cylinder containing Al-matrix together with Si-precipitate. Therefore, the data obtained give the direct evidence that the visible particles are really the Si-precipitates in the depleted Al-matrix.

The data obtained show that the magnetron sputtering cannot allow to get the supersaturated Al-Si solid solution. Obviously, the conditions during the deposition are too close to the equilibrium. On the other hand, it is shown that the twin construction of the cathode allows one to produce the spectrum of alloys with various content in one experiment and identical conditions. The construction of deposition apparatus allows one to use the same source both for magnetron sputter and vacuum arc deposition. The vacuum arc deposition is very well known as a method allowing one to produce the phase stable at the high pressures and metastable at the normal pressure (like diamond [12]). Therefore, it is reasonable to try in the future to produce the supersatured metallic alloys with the aid of vacuum arc deposition.

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