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Evaluation of crystalline germanium thin films electrodeposited on copper substrates from propylene glycol electrolyte

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Germanium thin films electrochemically deposited at 300K from a solution of $GeCl_4$ in propylene glycol were investigated using X-ray diffraction, infrared spectroscopy and atomic force microscopy. XRD reveals that the germanium electrodeposits are of crystalline structure and have the preferred crystallographic growth orientation [220]. The presence of the hydrogen bonding in the germanium films such as Ge-H and Ge-H_2 is shown from the IR absorption and does not cause a phase transition from crystalline structures to amorphous structures. The AFM images exhibit anomalous surface roughening behaviors in growth that deviate from statistical surface growth models and indicate a transition from rough surfaces to smooth surfaces.

Keywords: germanium, electroplating, X-ray diffraction, infrared spectroscopy, AFM, roughness

1. Introduction

Germanium-based materials in use for light emitting devices [1], infrared sensors [2] and solar cells [3] have been an active area of research for a past decade. The germanium-based thin films are prepared mainly by vapor deposition such as sputtering and chemical vapor deposition. Unfortunately, except for some studies [4-6] made decades ago, there have been declines in interests in electrodeposition of germanium owing to a wide use for silicon in electronics [7]. However recently two studies on Ge nanocrystals [8-11] have been reported, which may lead to new possibilities of in-direct semiconductors. Takeoka et al. [8] reported that the band-gap of the Ge nanocrystals fabricated by RF sputtering increases with a decrease in the size. Endres et al. [9-11] investigated the growth process and the band-gap of the Ge nanocrystals, which were electrodeposited from ionic solutions, using in-situ STM.

The first attempt for electrodeposition of germanium from a solution of $GeCl_4$ in propylene glycol with was in past five decades made by Szekely [4]. Further studies of germanium films electrodeposited at similar experimental conditions were made by Kadaner and Shkhova [5], who reported the evolution of hydrogen in large quantities at cathode electrodes. In this paper, the hydrogen bonding in germanium electrodeposits, which has not be measured, will be reported. In addition, since the presence of chemical bonding between hydrogen and germanium may cause a phase transition from crystalline structures to amorphous structures, X-ray diffraction (XRD) will be employed to identify the structure of germanium electrodeposits.

In recent years, surface roughening in thin films grown by deposition has attracted much attention because the height fluctuation on the surfaces indicates scaling invariance both spatially and temporally [12, 13]. In electrodeposition [14-16], statistical growth models [12] have been applied to analyze scaling properties of electrodeposited thin films. Scaling invariance is characterized by scaling exponents related to surface growth mechanisms. The scaling exponents determine universality classes characterizing the scaling behavior of the surface growth mechanism and are independent of specific systems and insensitive to experimental conditions such as current density distribution and fluctuation of solution composition in electrodeposition. In this paper, the scaling behavior in surface roughening in germanium electrodeposition will be investigated using surface images observed by atomic force microscopy (AFM).

The purpose of this study is to report characterization of germanium thin films electrodeposited at 300K from a 5 volume % solution of $GeCl_4$ in propylene glycol using XRD, Infrared-absorption spectroscopy (IR) and atomic force microscopy.

2. Experiment

Copper plates with a purity of 99.9 wt% were prepared, which were electrochemically polished at an applied voltage of 1.7 V in a solution comprising H_3PO_4 70 ml, the distilled water 35 ml and gelatin 1.5 g [17]. The copper plate with a rms (root-mean-square) roughness of 3.8 nm, which appeared to be a mirror, was cleaned by a wet process. The rms roughness of the copper surface electrochemically polished was measured from the AFM image, which was much less than that of germanium electrodeposits. The copper substrate for cathode electrodes and graphite plate for anode electrodes were located parallel in a still bath containing 5 volume % $GeCl_4$ in propylene glycol. The water contained in propylene glycol produces hydrogen in electrodeposition. Propylene glycol that receives no treatment for purification was used because some effective methods for water removal were not found. At this point, ionic liquids used in Endres's experiments [9-11] as a solvent seem to have an advantage.

The bath was maintained at a temperature of 300 K and a fixed current density of 100 mA/cm^2 for 20-1000 sec. Szekely [4] reported a current density of 400mA/cm^2 as a best condition for electrodeposition of germanium. However, in our experiment at 400 mA/cm^2, bright metallic germanium deposits could not be obtained. A current density of 100 mA/cm^2 was selected from the appearance of the deposits. After electrodeposition, the solution adhered to the surface of electrodeposits was immediately washed with distilled water.

The deposit thickness was measured from the samples of the electrodeposited copper plates embedded in resin and sectioned using laser microscope that can be determined to an accuracy of the order of 0.23μm (Keyence,VF-7500, magnification250-2500). The hydrogen bonding configurations of the electrodeposits on the copper substrates were measured by Fourier transform infrared reflection spectroscopy (Perkin elemer, Spectrum 2000 Explore) within a wave-number range of 700-2200 cm^{-1}. X-ray diffraction (Shimazu XD-D1) was carried out to determine the structure and preferred crystallographic growth orientation of the germanium thin films. The electrodeposits were scanned in air with AFM (Shimazu SPM-9500) with a resolution of 512x512 pixels in contact with a sample surface. The tip radius of curvature dramatically affects the quality of the AFM images. The Si_3N_4 cantilever used in this study has a tip radius of 15nm, which gives a high resolution enough to observe germanium surfaces. The AFM images with different scan regions of 750x750 nm^2 and 1000x1000 nm^2 were used for calculations of the surface roughness.

3. Results and discussion

The germanium thin films electrodeposited for 20-1000 sec appeared to be mirror-like and had an average growth rate of 0.62±0.2 nm/s. The current efficiency was 1.0 % and the evolution of hydrogen at the cathode electrodes was observed during electrodeposition.

3.1 Crystalline structure

Crystallographic orientations of the germanium thin films grown on the copper substrates were determined using the X-ray diffractometer with a Cu-Kα target. The specimens used for X-ray diffraction were not germanium powders stripped off from the germanium electrodeposits on the copper substrates but as-deposited germanium thin films on the copper substrates. X-ray diffraction peaks were preliminarily measured at the diffraction angle 2θ ranging from 20 to 160 degrees. In consequence, only the (220) peak of germanium, and (111) and (200) peaks of copper were found. As shown in Fig.1, the diffraction peaks were again measured in detail at the diffraction angle in a range 30-70 degrees.

Fig.1 shows the typical X-ray diffraction pattern of the electrodeposited germanium film of 7.8μm in thickness, which comprises three reflection lines, the (220) line of the germanium film, and the (111) and (200) lines of the copper substrate. It can be seen that the germanium thin film grown on the copper substrate is of crystalline structure and has the preferred crystallographic growth orientation [110]. The X-ray diffraction measurement has been repeated several times and the results were consistent within experimental uncertainty. In consequence, one peak diffracted by (220) planes of germanium was found as shown in Fig.1. The peak diffraction angle θ produced by (220) planes is negatively shifted to approximately 0.4 degrees in comparison with 22.67 degrees in powder germanium diffraction patterns. This means the expansion of germanium, i.e. a little increase of the lattice constant, which may be due to the presence of the hydrogenated germanium. Propylene glycol used in this experiment contains 0.2 wt% water, from which the hydrogen gas is produced in electrodeposition. Water-free propylene glycol will be required for the crystalline germanium electrodeposit that is of importance for applications to electronics in comparison with amorphous germanium.

3.2 Hydrogen bonding in the germanium deposits

There have been very few reports about the hydrogen bonding in germanium electrodeposits. The hydrogen bonding in the germanium films electrodeposited on the copper substrates was measured by a Fourier transform infrared reflection technique.

The infrared reflection spectra of the germanium electrodeposit of 6.7 μm thickness are shown in Fig.2. The stretching modes of Ge-H and Ge-H_2 are widely recognized [1] to appear at 1870 and 1970 cm^{-1}, and the peaks at 755 and 820 cm^{-1} can be related to the bending modes of Ge-H_2. Hence, in Fig.2 the reflection band in the 2100-1700cm^{-1} wave number range is considered to be composed of two absorption bands, at 1870 and 1970 cm^{-1}. The valley around 800 cm^{-1} can be assigned to the bending mode comprising 755 and 820 cm^{-1} wave number. This indicates the presence of chemical bonds between germanium and hydrogen. Thus, the generation of Ge-H_n is found to take place in electrodeposition even at a temperature of 300K.

Kadaner and Shakhova [5] proposed germanium reduction at cathode electrodes,

$$2H_{ad} + Ge^{2+} \rightarrow Ge + 2H^{+}, \tag{1}$$

where H_{ad} indicates hydrogen atoms adhered on the cathode surface. However taking into consideration the presence of the hydrogen bonging, we can assume the following reaction:

$$(n+2)H_{ad} + Ge^{2+} \rightarrow Ge - H_n + 2H^{+}, \tag{2}$$

where n is an integer, 0,1 and 2.

In general, the presence of the hydrogenated germanium must be infinitely related to the structure of germanium electrodeposits, which may cause a phase transition from crystalline structures to amorphous structures. However, in this experiment, the germanium electrodeposits remain crystalline.

3.3 Surface morphology

The AFM images of the germanium surfaces with a region of 1000x1000nm^2 electrodeposited for four different growth times are shown in Fig.3. The vertical scale of each image with a resolution of 512x512 pixels was magnified by a factor of 4.1 in order to enhance viewing. The surface morphology appears to be a set of continuous mounds. The sizes of the mounds initially increase with time and the surface becomes very rough at 100sec. But at 300sec the mounds almost disappear and the surface becomes smooth. This means that gaps between the mounds should fill with germanium or hydrogenated germanium, which suggests a lager lateral growth rate than the vertical growth rate. In fact, for 20-100sec, the average lateral growth rate of the mounds is about 2.0 nm/sec, which is greater than the vertical growth rate of the mounds, 0.67

nm/sec. This is very different from usual surface roughening behaviors in electrodeposition. The growth process in electrodeposition is considered to follow a scenario that larger mounds cover smaller ones with time and the surface roughness increases with time. However in this study, the surface roughness decreases at the growth time beyond 100 sec.

In order to investigate quantitatively what are stated above, we calculate the interface width w(L,t) defined by the rms fluctuation in the surface height h(r,t), which has the form [12, 13],

$$w(L,t)=\left\langle \left[h(r,t)-\langle h(r,t)\rangle\right]^2\right\rangle^{1/2} \propto t^{\beta}, \tag{3}$$

where <...> is the spatial average over the measured area, L is the system size, and positive β is the growth exponent that represents the time-dependent dynamics of the surface roughness. Eq.(3) indicates that the interface width w(L,t) follows a power law of time t. Many experiments of electrodeposits [14-16] have supported the validity of Eq.(3).

There have been recently considerable efforts in understanding the phenomenon of surface roughening in film growth [12,13]. Generally it is recognized that the surface morphology and dynamics of growing surfaces by deposition obey simple scaling laws associated with scaling exponents such as the growth exponent β. For example, the KPZ equation [18], which is a kind of statistical surface growth models, is represented by

$$\partial h(r,t)/\partial t = \nu\, \nabla^2 h(r,t) + \lambda\left(\nabla h(r,t)\right)^2/2 + \eta, \tag{4}$$

where ν is the surface tension, λ the coefficient of the lowest order nonlinear term, and η reflects the random fluctuations in the deposition process. For the one-dimensional KPZ equation, β=1/3 is theoretically obtained.

Fig.4 shows a log-log plot of w(L,t) vs t for 20-1000 sec. The straight line best fitted to the data gives a value of β=1.8, which is inconsistent with any values predicted by statistical growth models [12]. It can be seen that after w(L,t) reaches the maximum value, w(L,t) decreases with time, which indicates a negative β. In general the theoretical value of β is 1/2 and under [12,13]. These anomalous behaviors can not be explained at present.

4. Conclusion

The germanium thin films electrodeposited at 300 K from a $GeCl_4$ solution in propylene glycol were investigated. XRD reveals that the germanium electrodeposits are of crystalline structure and have the preferred crystallographic growth orientation [110]. The presence of the hydrogen bonding in the germanium films such as Ge-H and Ge-H_2 is shown from the IR spectroscopy. The AFM images exhibit anomalous behaviors in the surface roughening of the germanium electrodeposits.

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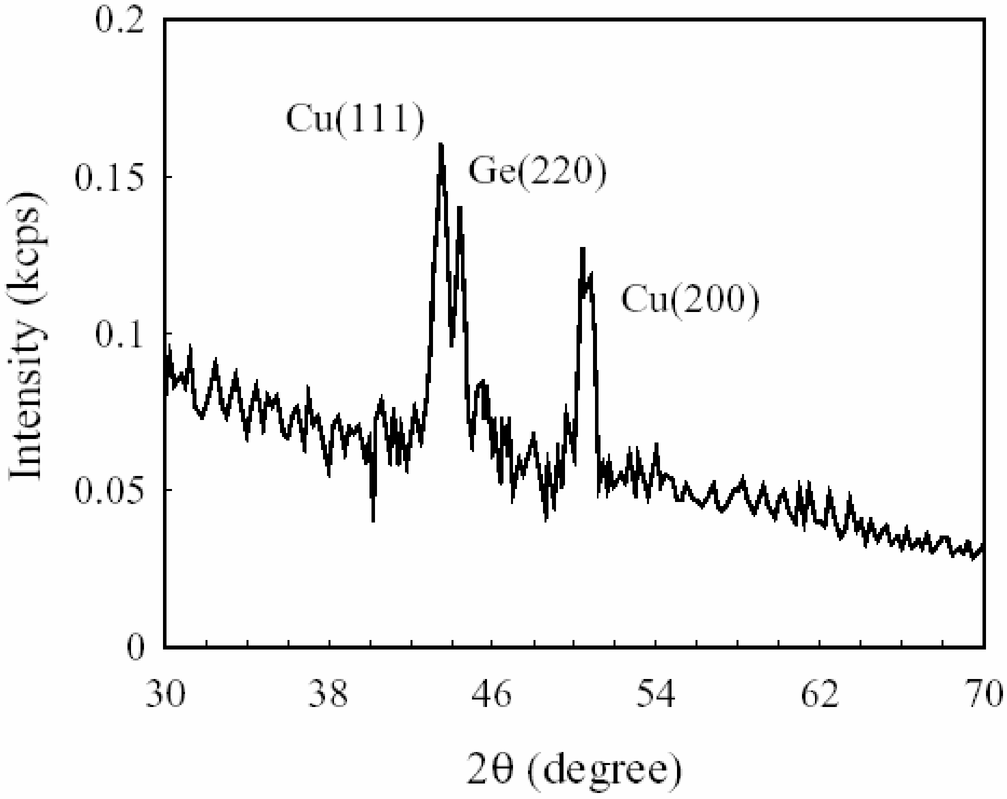
Figure Captions

Fig.1 Typical X-ray diffraction pattern of the electrodeposited germanium film. The characteristic X-ray CuKα was scattered by the germanium film of 7.8 μm in thickness using a standard θ-2θ diffractometer.

Fig.2 IR reflection spectra of the germanium film of 6.7 μm in thickness.

Fig.3 AFM images of the germanium thin film grown for (a) 40 sec, (b) 100 sec, (c) 300 sec, and (d) 1000 sec. Each image has an area of 1000x1000 nm^2. The vertical scale of each image with a resolution of 512x512 pixels was magnified by a factor of 4.1 in order to enhance viewing.

Fig.4 Log-log plot of $w(L,t)$ vs t for $L=1000$ nm. The interface width $w(L,t)$ was calculated from the AFM image of the electrodeposited germanium film.



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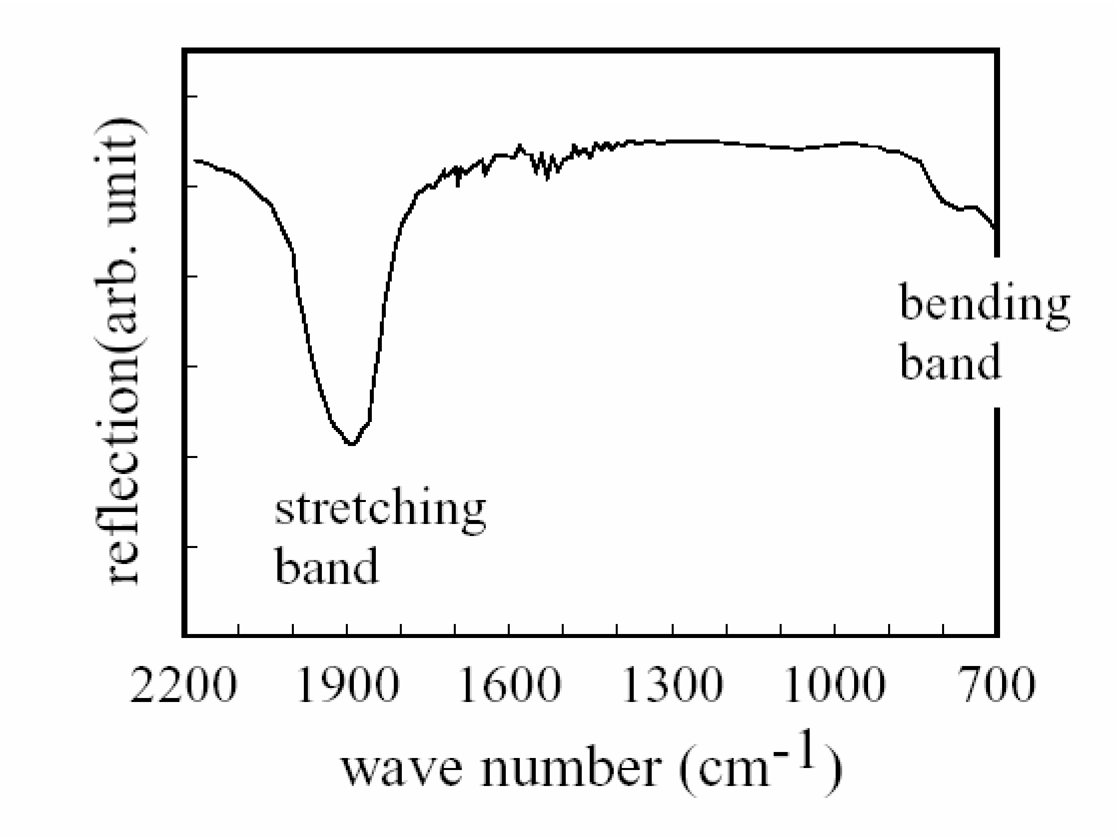

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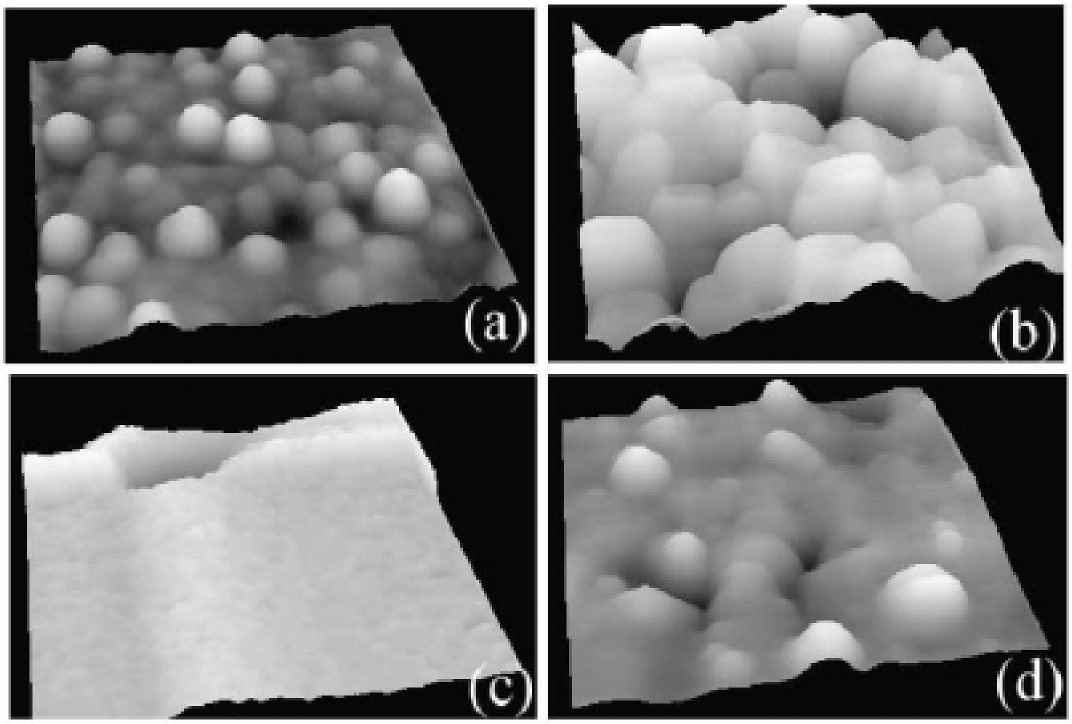

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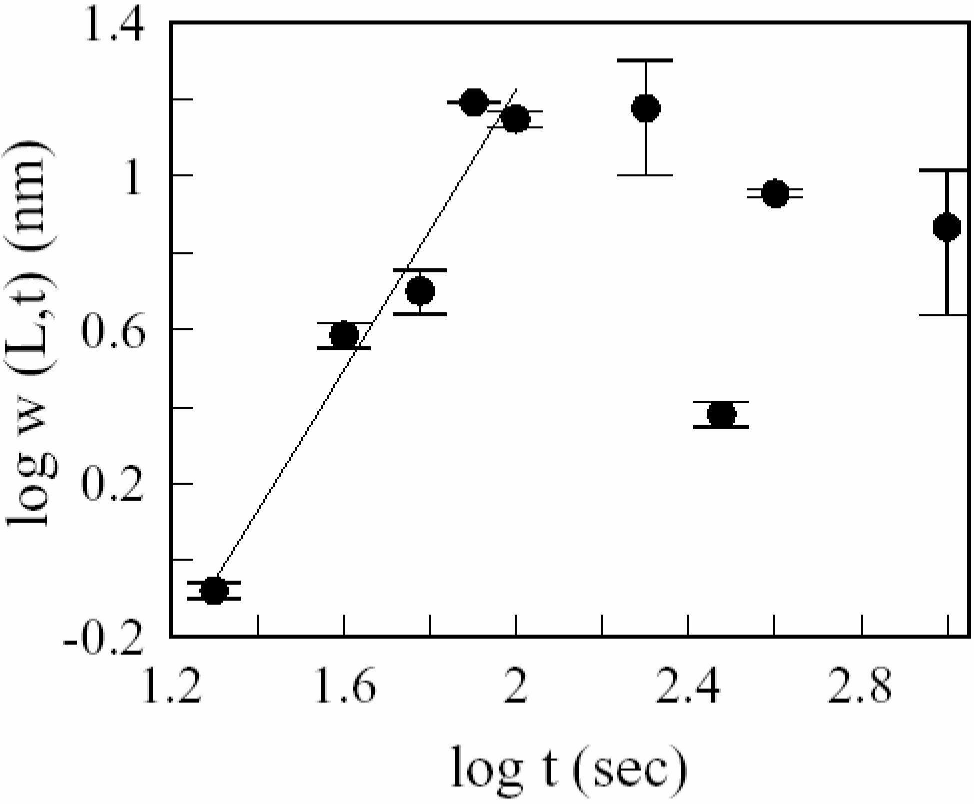

Fig.4 Log-log plot of w(L,t) vs t for L=1000 nm. The interface width w(L,t) was calculated from the AFM image of the electrodeposited germanium film.