Electrochemical Deposition of Ni into Mesoporous Silicon

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Nickel nanowires have been formed by the stationary electrochemical deposition of
nickel into mesoporous silicon from the modified Watts bath. The polycrystalline nature
of the Ni deposit has been established as well as expansion of its lattice parameter in
comparison with bulk nickel. Control of the potential of porous silicon during
electrochemical deposition allows to determine the moment of complete filling of pore
space with Ni. The maximum achieved filling factor was 67% of the pores. The pore
dimensions have been found to define the length and the diameter of the Ni nanowires
that have equaled to 10 um and 100-120 nm, respectively.

Introduction

Nanowires (NWs) of ferromagnetic metals incorporated in the porous matrix of a nonmagnetic
material have been the subject of intense research during the last decade as they may exhibit the
giant magnetoresistance effect of coherent spin waves (1, 2). Because of the large aspect ratio
(the ratio of the diameter of NWs to their length), the distinguishing feature of these nanoobjects
is their high magnetic anisotropy. All this together makes them promising for apllication in
magnetic memory devices with high packing density. To date, many studies have been performed
to obtain ferromagnetic NWs by using electrochemical deposition of metals in the matrix of
porous anodic aluminum oxide (3). Matrixes of porous silicon (PS) provide additional unique
features, since the diameter of the pores and the porosity of the channels can be varied in a wider
range than in the case of porous anodic aluminum oxide. In addition, the fabrication of PS and
metal filling of its matrix are in good agreement with the modern microelectronic technology
requirements. Studies on the electrochemical deposition of ferromagnetic metal in the PS were
started in the early 80's of the last century. The driving force behind this research was the idea of
getting thick layers of silicides by filling the channels of PS with metal followed by thermal
annealing. The first work (4) on the electrochemical deposition of nickel in PS was published in
1985. Several similar works have been carried out after that, which were summarized in a 1997
review (5). The first observation of the anisotropy of the magnetic properties of nickel nanowires
in the matrix of PS has been presented in (6). The use of PS as the matrix for different
nanocomposite structures has been the subject of active research. Recently the critical analyses
of the current state-of-the-art have been presented in (7, 8).

The aspect ratio and the filling factor are fundamentally important parameters of metal NWs
in the matrix of PS. Aspect ratio is the ratio of diameter to length of NWs. The filling factor is
the ratio of the metal mass effectively deposited into the porous layer to the metal mass, which
can be theoretically introduced into the pore channels of the matrix to provide a complete filling
with metal. The specific magnetization and anisotropy of magnetic properties are able to be
improved by increasing the aspect ratio and filling factor. Obtaining objects with an aspect ratio
of more than 100 and a filling factor of more than 25% is still challenging (8). Morphological
changes of the pore walls like dendritic branches as well as hydrogen evolution lead to
inhomogeneity of the metal deposit. It is very difficult to obtain homogeneous filling of the
pores. If the exchange of reagents within the pores is limited the channel might be blocked by the
accumulation of the deposited metal. This prevents uniform filling of the pores along its entire
length. One way to overcome this problem is to use a pulsed electrochemical deposition of metal

in PS. At the present time, using pulse mode allows Ni NWs in a matrix of PS with diameters ranging from 20 nm to 100 nm and a length of several microns (7, 8).

In this work Ni deposition into pores of mesoporous silicon under stationary galvanostatic regime from a modified Watts bath has been investigated. We have used PS samples of 72% porosity. The skeleton of such PS is known to be partially depleted of charge carriers. Reported results have shown surprisingly good filling of pores of 10 um length without using a pulsed mode.

Experimental

Antimony doped 100 mm monocrystalline silicon wafers with (100) orientation and 0.01 Ohm·cm resistivity were used as the initial substrates. Organic clean of the Si wafers was performed for 10 min with a hot (75 ^{o}C) solution of NH_4OH, H_2O_2 and H_2O mixed in a volume ratio of 1:1:4. Then the wafers were dried in a centrifuge and cut into a number of rectangular 3x3 cm samples. Just before PS formation each experimental sample was immersed into 5% HF solution for 30 s to remove the native oxide. Immediately after oxide removal, the Si sample was placed in an electrolytic cell made of Teflon. The active opening of the cell had a round shape and an area of 3 cm^2. Uniform PS layers were formed by electrochemical anodization of silicon samples in a solution of HF (45%), H_2O and $(CH_3)_2CHOH$ mixed in a 1:3:1 volume ratio. A spectrally pure graphite disk was used as a contact electrode to the back side of the samples during the electrochemical treatment. Platinum spiral wire was used as a cathode electrode. Anodization was performed at current density of 80 mA/cm^2 for 200 s. This regime provided formation of uniform PS layers with thickness of 10 um and porosity of 72%. Pore diameters of 100-120 nm and pore density of $2 \cdot 10^{10}$ cm^{-2} were estimated from the SEM images.

After PS formation the HF solution was removed and the electrolytic cell was thoroughly rinsed with deionized water for 5 minutes. The cell was then filled with electrolyte for the deposition of nickel. Nickel was incorporated into PS matrix by electrochemical galvanostatic deposition at constant current density of 3.5 mA/cm^2. The composition of electrolyte for Ni deposition was slightly different from that known for Watts bath. It consisted of 213 g/l $NiSO_4 \cdot 7H_2O$, 5 g/l $NiCl_2 \cdot 6H_2O$, 25 g/l H_3BO_3 and 3 g/l saccharin. At room temperature such electrolyte has pH = 2.6. Ni was deposited on five PS samples for 5, 15, 30, 60 and 80 min. Potential measurements were carried out using Ag/AgCl reference electrode filled with the saturated KCl solution. The reference electrode was immersed into a small bath filled with the solution for Ni deposition. This bath was connected with the electrolytic cell by a flexible polymer tube of 2 mm inner diameter ended with a Luggin glass capillary of 200 um aperture. Both the Luggin capillary and polymer tube were filled with the solution for Ni deposition. The Luggin capillary was placed on the surface of PS and defined a clear small sensing point for the reference electrode near the PS electrode. The equipment used to conduct electrochemical processes was the potentiostat/galvanostat AUTOLAB PGSTAT302. Gravimetric method was applied to determine the porosity of PS and the filling factor of Ni. Mass measurements were performed with Sartorius CP225D micro/analytical electronic balance. The instrumental error of mass measurements was about 10 ug.

The structure of the samples was studied with the scanning electron microscope (SEM) Hitachi S-4800. The elemental composition of samples was determined using SEM Cambridge Instruments Stereoscan-360 with a Link Analytical AN 10000 energy dispersive X-ray analyzer. The phase composition of the samples was determined by XRD using CuKα radiation in the X-ray recording on the points.

Results and discussion

One of the important tasks of the electrochemical deposition of nickel (and other metals) in PS is determination of the specific time points, which correspond to different filling stages. The moments of Ni precipitation on the PS surface and the complete filling of the whole pore space are especially important. To solve such problem the applied electrochemistry offers measurement of the potential of PS during the deposition in galvanostatic mode at a constant cathode current. The measurement of PS potential as a function of deposition time may provide considerable insight on the different deposition behaviors (9).

Figure 1 shows PS potential dependencies on deposition time for five PS samples with 10 um of porous layer thickness and 72% of porosity.
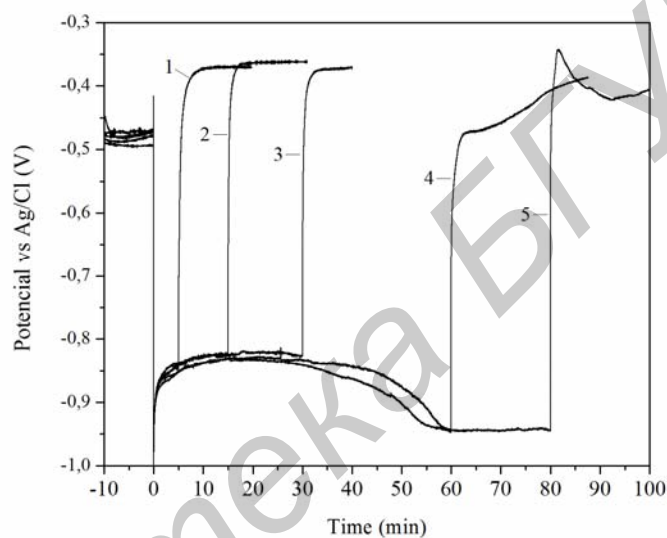

Figure 1. The potential of PS vs. time of nickel electrochemical deposition. Deposition process was stopped at different times: (1) – 5 min, (2) – 15 min, (3) – 30 min, (4) – 60 min, (5) – 80 min.

When the electrolytic cell with PS sample was filled up with the solution for Ni deposition, the Luggin capillary was also placed on the surface of PS. Measurement of the PS potential was started immediately after filling the cell with the electrolyte and the cathodic current was applied 10 min later. Ni was deposited in PS during different periods of time: 5, 15, 30, 60 and 80 minutes for samples 1, 2, 3, 4 and 5, respectively, as marked in Figure 1. After stopping the deposition (these points correspond to the decreasing spikes of the potential) the potential was recorded a while longer. Good reproduction of the time dependence of the potential was established for all five samples. The value of potential in the electrolyte without external polarization was almost constant in time and fluctuated around - 0.475…- 0.485 V. It indicates no appreciable change in reactions on PS surface, i.e. the surface of PS is stable in the Watts solution and does not change (9). At the moment of the current switching the sharp increasing of PS potential up to - 0.975…- 0.98 V was observed. Than potential gradually reduced and in 12 min reached permanent value about - 0.83…- 0.84 V. Half an hour later PS potential again started slow rising which stopped at 55-60 min at the value of - 0.95 V. Further deposition did not change this value. Current switched off at 5, 15 and 30 min (curves 1, 2 and 3) led to the immediate potential decreasing to - 0.37…- 0.375 V which was not affected by extract in electrolyte without any current. The same reduction of potential was observed after current stop at 60 and 80 min (curves 3 and 4) but it took more than 30 min to reach constant value of - 0.38

V. Below it will be shown that such potential behavior after 60 min of process indicates a full coverage of PS surface with Ni.

To study filling process of PS with Ni we have used SEM of cross sections of the experimental samples after different periods of the metal deposition. For example, Figure 2 presents SEM images of the top, middle and bottom parts of cross sections for 1, 2 and 3 samples (5, 15 and 80 min of the Ni deposition, respectively). In the top area of sample 1 (Fig. 2 a) the only single nanoparticles of nickel are observed on the pore walls. In the central part of the sample 2 (Fig. 2 b) NPs of 30-50 nm in diameter might be seen. The average number of NPs is about 5-7 per 1 um of pore length. The bottom image of the sample 1 (Fig. 2 c) shows the interface between PS and monocrystalline Si. It is characterized by significant increase of NPs amount to several tens per 1 um. Such fact means the metal deposition process began in the bottom of the pore channels. The careful analysis of the SEM images of the sample 1 (Fig. 1 a, b, c) revealed primary Ni NPs nucleation occurred on the tips of PS skeleton branches. We suggested that it was caused by high local current density due to accumulation of electric field on the tiny ends of PS parts. The pore enters were not blocked as well as Ni deposition on the outer surface of PS did not take a place. The filling factor of pore space with Ni for the sample 1 was estimated by the gravimetric method as 4.5 %.
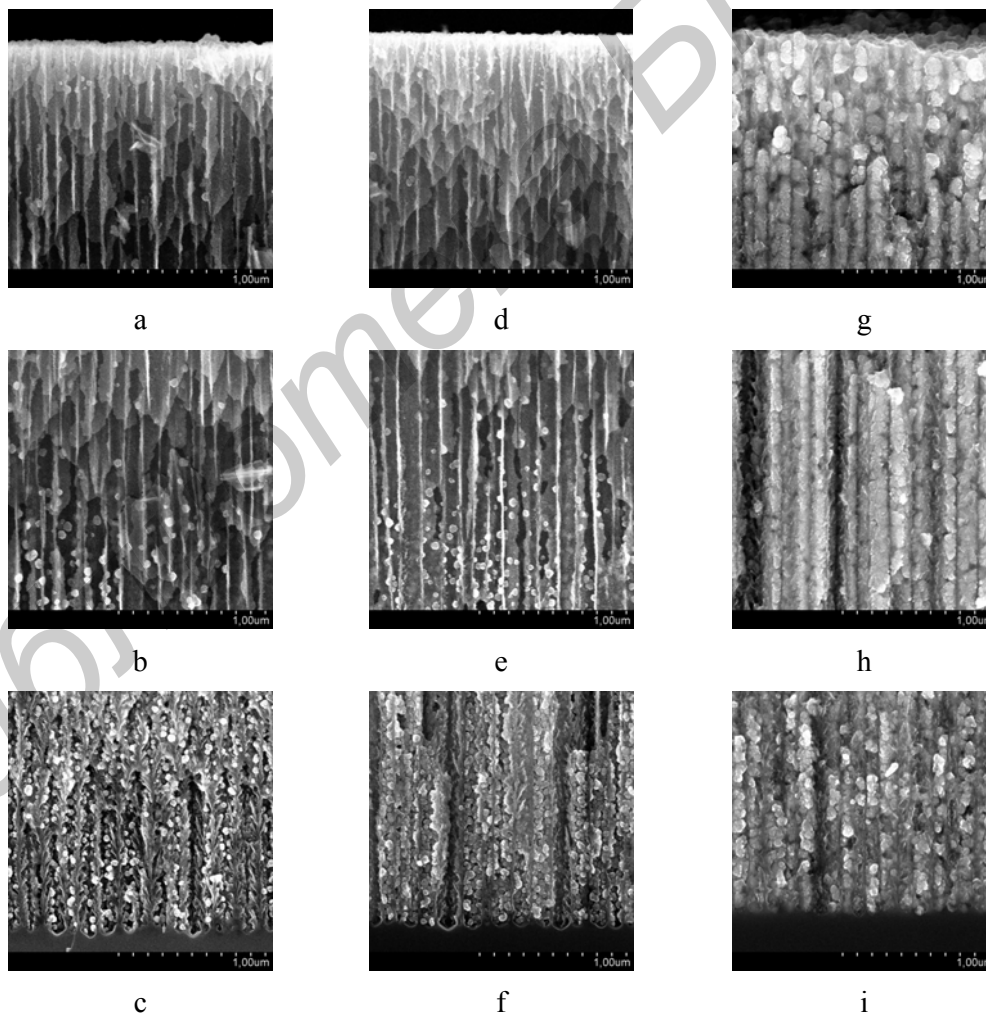

Figure 2. SEM images of the top (a, d, g), middle (b, e, h) and bottom (c, f, i) regions of cross sections of PS samples subjected to the nickel deposition during different times: (a, b, c) – 5 min, (d, e, f) – 15 min, (g, h, i) – 80 min.

Figure 2 (d, e, f) shows SEM pictures of cross section of the sample 2 (15 min of deposition). The top and the middle regions of PS (Fig. 2 d) look like the same areas of the sample 1 but are characterized by a larger number of NPs. However, in the bottom part we may see great differences. The dimensions of Ni NPs are about 40-70 nm as in the center but their number is several times more. Moreover, Ni NPs are connected and form quasi continuous wires. The filling factor of pore space with Ni for the described sample was about 23%.

Figure 2 (g, h, i) presents SEM cross sections images of the sample 5 which was obtained by the Ni deposition in PS during 80 min. The outer surface of the sample was covered with continuous nickel film of 2 um thickness. This upper Ni layer was removed by the scalpel before sample cutting for SEM analysis. As it might be seen pore channels in this case are well filled with metal NWs. Ni wires consist of large conglomerates that are in close contact with each other. On the top of the cross section grown together particles are distinguished. The diameter of particles varies in the range from 100 to 120 nm. It should be noted that pretreatment of the sample, resulting in the exfoliation of the surface layer of Ni, could destroy the Ni NWs in the upper part of the sample. In the middle of the sample 5 nickel wires are rather monolithic and their diameter is 100-120 nm. It corresponds exactly to the diameter of the pore channels. At the bottom of the sample 5 the quality of nickel filling is lower than in the central part. It is possible to see the individual particles of nickel. Filling factor was estimated as 67%, which is in a very good agreement compared with the known data (8).

To prove Ni nature of NWs observed on SEM pictures, XRD analysis has been carried out. Figure 3 shows XRD profiles of PS after Ni electrochemical deposition during 5, 30 and 80 min (samples 1, 3 and 5, respectively). The angles varied in the range $20^0 \le 2\theta \le 90^0$. It is known that polycrystalline nickel has cubic crystal cell with the lattice parameter a = 0.3522 nm (10). As seen from Figure 3 each diffraction curve has reflexes corresponding to the major crystallographic planes of Ni such as (111), (200) and (220). It means that the deposited in PS matrix Ni has polycrystalline nature. PS matrix itself resulted in a wide peak of the high intensity which appeared at the angle responsible for the silicon (400). Calculated lattice parameter a of the nickel NWs is 0.4-0.5% higher than that of polycrystalline nickel powder and vary in the range $0.3537 \le a \le 0.3541$ nm. Such expansion of the crystal lattice of nickel NWs might be explained by the influence of the PS matrix which has cubic cell, but with larger lattice parameter $a_{Si} = 0.5431$ nm. As a consequence, the crystal lattice of the Ni which was growing inside of PS pores was expanded.

Detailed study of the kinetics of Ni deposition in the PS matrix required X-ray microanalysis of the samples by scanning of the cleavage surface with an electron beam of SEM Stereoscan-360. The profile of distribution of the Ni concentration from the surface to the bottom of the porous layer was obtained. Results of the analysis are shown in Figure 4. We analyzed the profiles of nickel in PS (Fig. 4) and data on the structure of the samples (Fig. 2) for different times of Ni deposition and proposed the following model of the nickel NWs growth. At the initial stage (sample 1) Ni NPs nucleation and development began in the bottom region of PS (depth of 8-10 um from the surface) on the tips of branches of the PS skeleton. During the deposition (sample 2) the size of nickel particles increased to 40-70 nm as well as their number in the central part of PS.

During the deposition process we observed the number of nickel particles increasing while its dimensions rose very slightly at the center and the bottom of PS. This led to the almost complete filling of pore channels. After 60 min of the deposition Ni NPs grew together and almost completely filled the pore space. It might be proved by constant potential value - 0.95 V. Prolonged deposition time caused Ni layer deposition on the outer surface of PS (sample 5).
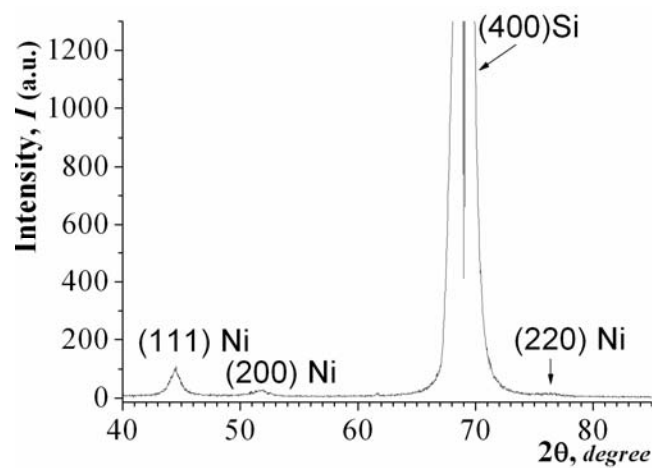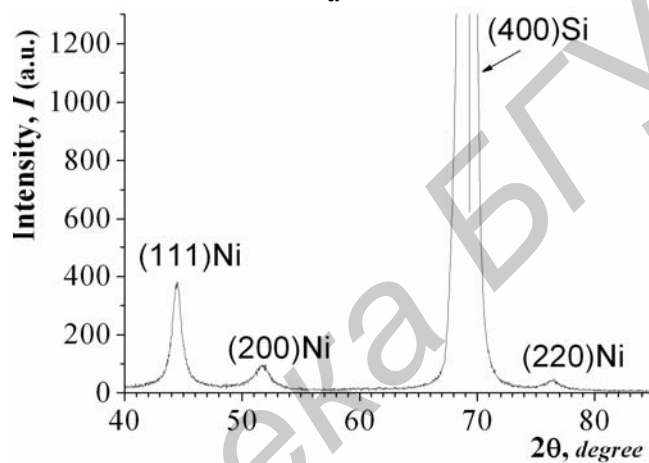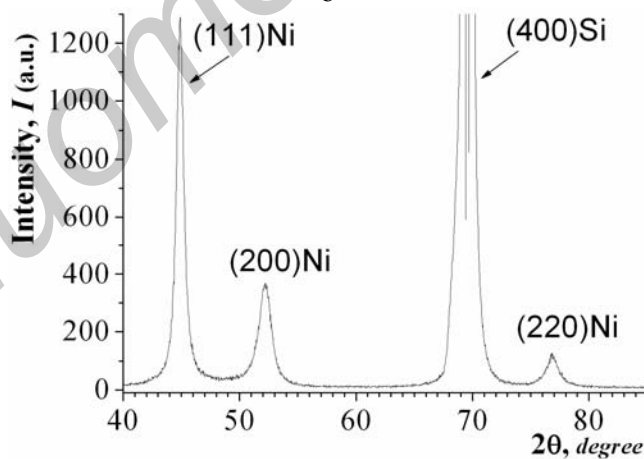
Figure 3 . XRD profiles of PS subjected to the nickel electrochemical deposition during (a) – 5, (b) – 30 and (c) – 80 min.

General consideration of the obtained results allowed summarizing that the PS potential stabilization after 60 min of the Ni electrochemical deposition has been connected with complete filling of the pore space by metal. At this moment Ni continuous film has started to form on the outer surface of PS layer. Such experimental fact is promising for control of the PS filling level during PS/Ni nanocomposite formation.
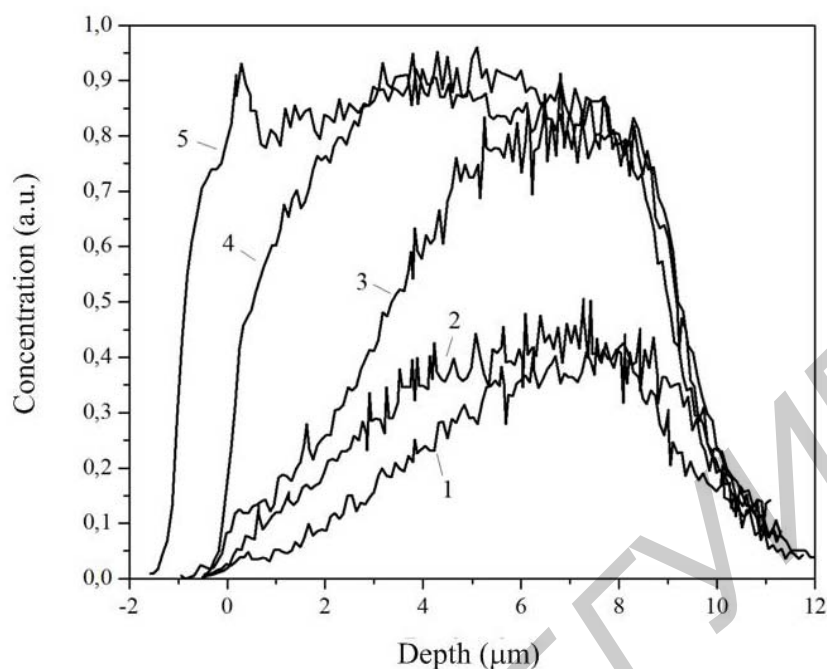
Figure 4. Nickel concentration profiles in PS samples determined by X-ray microanalysis. Nickel deposition time: (1) – 5 min, (2) – 15 min, (3) – 30 min, (4) – 60 min and (5) – 80 min.

Conclusion

Stationary regime of the nickel electrochemical deposition into matrix of the mesoporous silicon from the Watts bath has been found to obtain continuous Ni NWs. According to the SEM analysis the length and the diameter of NWs have been set by PS structural parameters and are equal to 10 um and 100-120 nm, respectively. The polycrystalline nature of the Ni NWs has been established by XRD. The lattice parameter of Ni NWs has been determined to be expended on 0.4-0.5% in comparison with bulk nickel. Such increasing is significant for cubic dense packing of Ni atoms and might be explained by PS matrix influence. The stages of Ni deposition process from nucleation through separated NPs growth to their coalescence in NWs have been carefully studied. The time required for the complete filling of pore channels has been fixed at 60 min of electrochemical deposition. Proposed PS substrate and regimes of the Ni deposition have allowed achieving the maximum value of the filling factor about 67%. Moreover, observation under the PS potential during electrochemical deposition has been found to control the filling process of pore space with Ni.

Recently magnetic anisotropy of the easy axis type along the NW orientation direction has been observed for the NWs formed in PS (11). At the present time further research of the magnetic properties of Ni NWs incorporated into PS is carrying out.

Acknowledgments

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