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Abstract

The paper presents technology for a phased low-temperature diffusion doping of silicon with Holmium that helps engineer clusters of impurity atoms distributed across the entire bulk material. The authors have shown that no surface erosion or formation of alloys and silicides on the surface are detected while applying low temperature diffusion technology which normally takes place during high-temperature diffusion doping. The authors revealed the increased thermal and radiation resistance of silicon samples containing clusters of impurity atoms of Holmium.

Key words: Holmium, technology, cluster, erosion, low temperature diffusion, doping, heat resistance, degradation.

INTRODUCTION

Currently, in the field of physics of semiconductors the activities aimed at engineering a novel type of material by forming clusters on the surface and in the bulk silicon material that change its fundamental parameters are in great demand. The development of a technology for the formation of clusters of impurity atoms, which allows one to create nanoscale structures in a crystal bulk with a sufficiently high concentration and given composition, structure, and physical parameters, is one of the main tasks of modern microelectronics [1-5].

The semiconductors with engineered bulk structures, especially with clusters of impurity atoms, are of great scientific and practical interest. In such materials, a number of new physical phenomena have been discovered that make are expected to make a great impact on the development of modern micro- and nanoelectronics. In this regard, the formation of clusters of rare-earth impurity atoms is of particular interest [6–8] to many researchers worldwide.

The above research is relevant due to the existence of a number of unresolved issues from the point of view of developing a technology for the formation of clusters of impurity atoms of rare-earth elements with a controllable structure and properties in a silicon lattice, which is one of the urgent and promising problems of modern nanoelectronics. Clusters of impurity atoms of rare-earth elements in silicon not only allow one to control the fundamental parameters of silicon and its magnetic properties, but also reveals a number of new unknown physical phenomena in it, the use of which opens up new possibilities for developing instruments with unique technical characteristics.

RESEARCH METHODOLOGY

By using microprobe analysis (Jeol Super Probe JXA-8800 R/RL), IR microscopy (INFRAM-I), and AFM (Dimension 3000), the authors have been able to study the process of formation of clusters of Holmium atoms. Also changes in their structure, size, and density were also studied. The electrophysical parameters of the samples were measured using the four-probe method and the Hall effect method. Based on theoretical calculations, the concentrations of doped impurity atoms that

participate in cluster formation were determined.

The impurity atoms of Holmium in the bulk of the silicon crystal lattice were investigated using an INFRAM-I-type infrared microscope. The INFRAM-I infrared microscope ensures accurate observation of not only the surface of a silicon sample, but also makes it possible to study all its layers, thus enabling us to examine the sample across the entire bulk.

To measure the lifetime of minority charge carriers, the authors have used the technique of transients of a large amplitude sinusoidal current. The choice of this technique was dictated by the fact that the investigated Si <P,Ho> material as well as the reference samples, tended to change their resistivity in a rather wide range during heat treatment, so the use of standard pulsed methods made it difficult to obtain reliable information. The error of the measurements was not more than 5%.

RESULTS AND DISCUSSIONS

Phosphor-doped n-type silicon and Boron-doped p-type single crystal silicon samples grown by the Czochralski method, where the concentration of residual oxygen was $6 \times 10^{17} \text{ cm}^{-3}$, with a resistivity in the range of $\rho = 1-100 \text{ } \Omega \cdot \text{cm}$, were used as starting material. The thickness of the initial silicon samples was approximately 380 μm . Holmium was used as dopant. Doping of the samples was carried out in evacuated pumped-out quartz ampoules from a thin metal layer sprayed in vacuum on the surface of silicon samples. In separate ampoules, under similar conditions, reference silicon samples were annealed without Holmium atoms to evaluate the effect of diffusion doping on electro-physical parameters of the samples. The mechanical and chemical treatment of all samples were carried out under identical conditions.

While studying topology of clusters of impurity atoms of Holmium, the authors note that the picture manifests not just random accumulation of a certain number of atoms of a certain impurity somewhere in the lattice. This is a local semiconductor region enriched in impurity atoms, which, as a rule, has a clearly defined structure with an ordered arrangement of both impurities and basic matrix atoms. The impurity atoms in clusters themselves are part of a sub-lattice with a specific arrangement of atoms and ions, correlated with the lattice of the semiconductor, which explains their relatively high stability.

Under external influence, clusters of impurity atoms can change their state. Searching for ways to control the state of clusters and their ordering in the crystal lattice of a semiconductor is of great scientific and practical interest. This interest is partly explained by the fact that there is a possibility to engineer bulk nanostructured semiconductor materials.

Another possibility is obtaining new types of photonic materials and bulk superlattices with tailored parameters. The study of semiconductor materials with ordered distribution of clusters of impurity atoms as a whole allows us to determine their unique functional capabilities.

The "low temperature diffusion doping" technique was first explained in [10]. The dopant and samples are put into a pumped-out quartz ampoules (pressure in the ampoule is $\approx 10^{-6}$ mm of Hg column). They are slowly inserted into a diffusion furnace at $T = 300\text{K}$. It was established in advance that the temperature of the furnace in time of inserting an ampoule would gradually increase at rate of 5 deg./min. Thereafter, the samples would be heated up to $T = (550-700^\circ\text{C})$ and maintained at this temperature for $t = (10-20)$ min, then the furnace temperature would be risen quickly at rate of (150-200 deg/min) up to a certain temperature of $T = 1200-1250^\circ\text{C}$ and then at this temperature

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the samples would stay for a certain duration, after which the ampoules would be removed from the furnace and cooled at a speed of 2000/sec.

Capacity, correctness and reliability of the proposed doping technology can be verified only after positive answers to the following questions:

Do impurity atoms manage to diffuse to the required depth of a sample and what is this depth?

Is the concentration of embedded impurity atoms sufficient to have a significant effect on the properties of a sample?

What are the surface and near-surface state of the samples after diffusion, reproducibility and effectiveness of this technology?

The technology should provide for formation of clusters of impurity atoms in the silicon lattice and ensure stability of such clusters.

The answers to these questions were obtained experimentally:

The above diffusion doping was carried out tens of times. After each diffusion, 5 to 7 samples were obtained, the surface of which was examined by an IR microscope. Diffusion was also carried out by applying the traditional technique. As the results of the study had shown, in contrast to samples obtained by the traditional technique, there was virtually no surface erosion, no formation of alloys and silicides both on the surface and in the surface region of the new samples.

To determine the depth of impurities layer during the diffusion doping process, we studied the resistivity of the samples by using the 4-probe technique across the thickness of the samples, as well as determined the concentration of charge carriers and mobility by the Hall effect technique.

On the basis of the experimental results, it can be argued that in the low-temperature region, diffusion does occur along interstitial sites, and impurity atoms are in interstitial states. An additional proof of this assumption can be the fact that, at low-temperature diffusion, the calculated concentration of vacancies will be $N_v \approx 10^7 \text{ cm}^{-3}$, i.e., almost 7-8 orders of magnitude lower than the concentration of impurity atoms in the interstices.

One of the important conclusions from these experimental results is that the diffusion mechanism and the concept of solubility of impurity atoms under conditions of low-temperature diffusion differ significantly from those during the diffusion at high temperatures, and the main diffusion parameters and solubility obtained in this case require substantial adjustment.

As proven by the above experiments, the new technology, in addition to the above scientific novelty, also has a number of important practical advantages:

- the time of the diffusion process is reduced by 2-2.5 times
- the energy consumption for diffusion is reduced by 2 times
- the formation of various alloys, silicides, both on the surface and in the surface region and surface erosion are almost completely eliminated.

All these advantages of the new technique of diffusion doping allow not only to simplify the technology for producing samples, but also to form clusters of impurity atoms.

After polishing the surface of the samples, the state of the clusters of Holmium atoms was studied using an INFRAM-I infrared microscope. To make sure that the formation of clusters occurs throughout the entire volume of the crystal, the samples were subjected to layer-after-layer (each 5 μm) grinding, starting from the surface of the crystal to down to half the thickness of the sample and each time the samples were again polished and examined using an IR microscope.

As shown by the results of infrared microscopic studies, in all samples, regardless of the type and concentration of the initial impurity atoms, the researchers have been able to observe uniformly

distributed dark points of clusters of Holmium atoms of size $d=2\div 15\ \mu\text{m}$. Figure 1 represents a micrograph of a silicon sample doped by Holmium by implementing the traditional high-temperature diffusion doping technology. As can be seen from the figure, in the sample doped with Holmium by traditional technology, cluster formation does not occur.

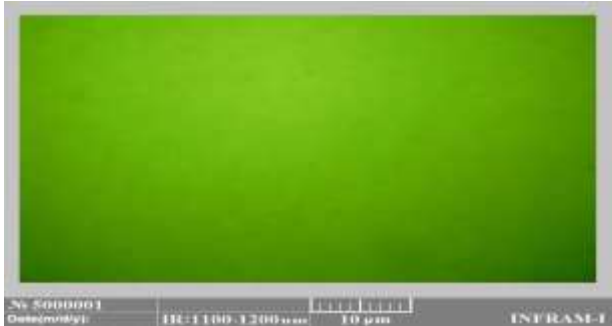


Figure 1. A micrograph of the silicon sample doped with Holmium atoms by using traditional high-temperature diffusion technology.

A micrograph of the surface of a silicon sample doped with Holmium by using optional staged low-temperature diffusion doping technology is shown in Figure 2.

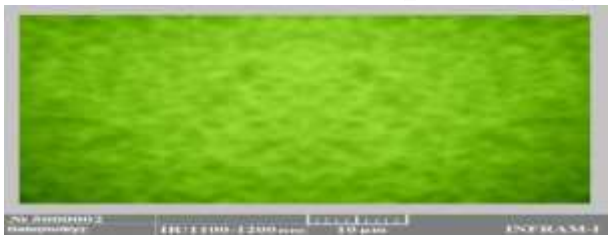


Figure 2. A micrograph of the silicon sample doped with Holmium by using optional staged low temperature diffusion doping technology

We found that during staged low-temperature diffusion, the temperature and time of diffusion affects not only the depth of penetration of the impurity, but also the size of the forming clusters, and can also cause them to not form. In fig. Figure 3 shows a micrograph of a silicon sample obtained by two stage diffusion of Holmium at relatively low final temperatures and holding times



Figure 3. Micrograph of the silicon sample obtained by two-stage diffusion of Holmium at relatively low final temperatures and retaining intervals.

As can be seen, the number of clusters is very negligent, and their sizes are small, which are of the order of hundreds of nanometers. With a further increase in the number of diffusion stages, their duration, and temperature, large clusters of impurity atoms of Holmium of several microns in size are formed, uniformly distributed across the entire bulk of the sample. Somewhat

interesting results were obtained by using three-stage diffusion doping process. In this case, clusters were formed with the participation of defects in the crystal lattice of silicon (Fig. 4).

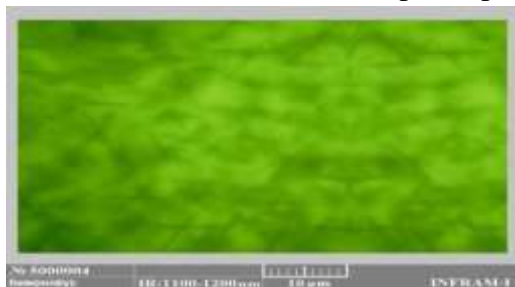


Figure 4. Micrograph of the silicon sample obtained by three-stage diffusion doping with Holmium atoms at relatively high final temperatures and long retaining times.

It was determined that, in silicon samples (thickness 380 μm), Holmium penetrates to a depth of 60 μm from the surface, and clusters are formed in a layer 50 μm thick and were distributed uniformly throughout the thickness. The study of the influence of low-temperature annealing on the size and distribution of clusters showed that upon annealing in the temperature range 600 \square 800 $^{\circ}\text{C}$, ordering and enlargement of clusters of impurity Holmium atoms is usually observed.

In order to assess possible effects of clusters of Holmium atoms on performance specifications of effective solar cells, it is necessary to have information about their influence on the lifetime of minority charge carriers. Such studies are also of particular interest for revealing the state of clusters of Holmium in the matrix and their interaction with other impurity atoms and defects. Therefore, to study the lifetime of minority charge carriers, we chose Holmium-doped silicon with a concentration of $\text{N}_{\text{Ho}} \approx 10^{17} \text{ cm}^{-3}$.

The investigated samples after each stage of heat treatment under identical conditions were treated in a polishing etchant, which made it possible to remove oxide layers and other defects from the surface that normally appear during the heat treatment.

In Fig. 5 “the lifetime of minority charge carriers as a function of the annealing time” curve at $T=1000^{\circ}\text{C}$ for Si $\langle\text{P},\text{Ho}\rangle$ and reference samples are shown. The relative change in the resistivity of Si $\langle\text{P},\text{Ho}\rangle$ ($\text{N}_{\text{Ho}}=10^{17} \text{ cm}^{-3}$) of the time of additional thermal annealing at $T = 500^{\circ}\text{C}$ is shown in Fig. 6.

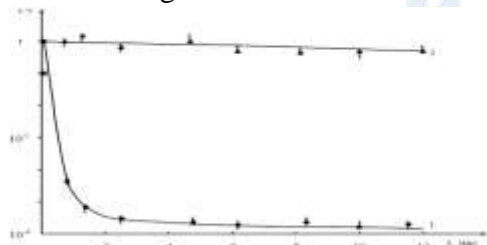


Figure 5. The dependence of the lifetime of minority charge carriers on the time of thermal annealing at $T = 1000^{\circ}\text{C}$. 1- Si $\langle\text{P}\rangle$; 2- Si $\langle\text{P}, \text{Ho}\rangle$.

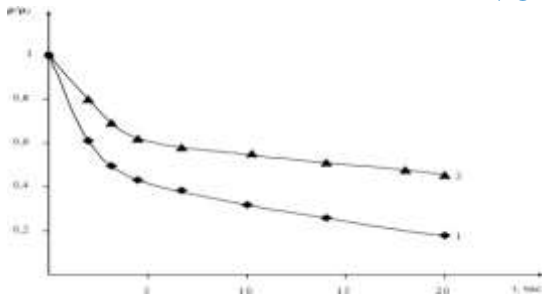


Figure 6. The relative change in the resistivity of the sample as a function of additional thermal annealing at $T = 500\text{ }^{\circ}\text{C}$. Samples: 1- initial Si <P>; 2-Si<P, Ho> ($N_{Ho}=10^{17}\text{ cm}^{-3}$). Table 1 shows the values of τ for the samples as a function of the annealing temperature. The annealing time is $t = 5$ hours. As can be seen from table 1, in the samples Si <P, Ho> the lifetime of minority charge carriers in a wide temperature range is quite stable. It should be noted that in samples Si<P, Ho> increase in τ is observed in comparison with the initial values. These results show that the presence of impurity atoms of Holmium almost completely suppresses the generation of recombination centers, which always exist in the bulk material, and are always generated in single crystals during heat treatment. It has been established that Si <P, Ho> samples are characterized by increased radiation resistance.

Sampel	Annealing temperature, $^{\circ}\text{C}$.				Annealing time, hour
	1000 $\square, \mu\text{s}$	1100 $\square, \mu\text{s}$	1150 $\square, \mu\text{s}$	1200 $\square, \mu\text{s}$	
Si<P, Ho>	15-20	20-30	25-40	25-35	5
Si<P, Ho>	17-25	17-35	20-35	20-40	5
Si<P, Ho>	16-20	14-25	25-40	20-40	5
Si<P, Ho>	15-25	16-30	20-40	25-40	5
Si<P, Ho>	10-20	20-30	22-38	20-40	5
Si<P>	less than 1 μs	less than 1 μs	less than 1 μs	less than 1 μs	5
Si<P>	less than 1 μs	less than 1 μs	less than 1 μs	less than 1 μs	5
Si<P>	less than 1 μs	less than 1 μs	less than 1 μs	less than 1 μs	5

As can be seen from Figure 6, the lifetime of minority charge carriers for all types of materials before heat treatment was approximately the same order of magnitude (16-32 μs), the lifetime of minority charge carriers in reference samples decreases sharply, during heat treatment for 1÷1.5 hours down to units μs . At the end of the heat treatment, τ becomes less than one microsecond. Meanwhile, the lifetime of minority charge carriers in the samples Si <P, Ho> practically remains constant for all heat treatment times. Table 2 shows the change in the electro-physical parameters

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of Si <P, Ho> samples before and after γ -irradiation with a dose of 109 R.

Thus, one can say that silicon doped with Holmium stabilizes the lifetime of minority charge carriers during additional thermal annealing, and also has the increased radiation resistance during γ -irradiation.

Table 2. Change in the electro-physical parameters of samples under γ -irradiation with a dose of 109R

Sample	Before annealing		After annealing		
	$\rho, \Omega \cdot \text{cm}$	n, cm^{-3}	ρ / ρ_0	n/n_0	$K_n = (n_0 - n) / F$
Si<P>	18,3	$2,4 \cdot 10^{14}$	$2,9 \cdot 10^{-3}$	$4,9 \cdot 10^{-4}$	$5,2 \cdot 10^{-5}$
Si<P>	18,8	$2,6 \cdot 10^{14}$	$3,05 \cdot 10^{-3}$	$4,6 \cdot 10^{-4}$	$5,6 \cdot 10^{-5}$
Si<P>	20,2	$2,36 \cdot 10^{14}$	$3,2 \cdot 10^{-3}$	$3,8 \cdot 10^{-4}$	$5,9 \cdot 10^{-5}$
Si<P>	21,7	$2,2 \cdot 10^{14}$	$3,36 \cdot 10^{-3}$	$3,4 \cdot 10^{-4}$	$6,06 \cdot 10^{-5}$
Si<P>	23,1	$2,15 \cdot 10^{14}$	$3,56 \cdot 10^{-3}$	$3,6 \cdot 10^{-4}$	$6,1 \cdot 10^{-5}$
Si<P>	24	$2,0 \cdot 10^{14}$	$3,7 \cdot 10^{-3}$	$2,5 \cdot 10^{-4}$	$6,23 \cdot 10^{-5}$
Si<P, Ho>	22,3	$2,1 \cdot 10^{14}$	1,3	$7,43 \cdot 10^{-1}$	$1,27 \cdot 10^{-5}$
Si<P, Ho>	22,4	$2,15 \cdot 10^{14}$	1,36	$7,35 \cdot 10^{-1}$	$1,32 \cdot 10^{-5}$
Si<P, Ho>	22,5	$2,2 \cdot 10^{14}$	1,42	$7,3 \cdot 10^{-1}$	$1,2 \cdot 10^{-5}$
Si<P, Ho>	22,6	$2,25 \cdot 10^{14}$	1,4	$7,1 \cdot 10^{-1}$	$1,35 \cdot 10^{-5}$
Si<P, Ho>	22,8	$2,3 \cdot 10^{14}$	1,405	$7,05 \cdot 10^{-1}$	$1,39 \cdot 10^{-5}$
Si<P, Ho>	22,9	$2,3 \cdot 10^{14}$	1,41	$7,0 \cdot 10^{-1}$	$1,4 \cdot 10^{-5}$

The positive effect of additional doping with Holmium is that any thermal annealing that causes the generation of thermal donors and undesired activation of impurity atoms leads clusters of Holmium atoms to remove the stress field and

brings the system to an equilibrium state, i.e. to increasing the entropy of the system. This can be confirmed by the results of additional experiments conducted in our laboratory by applying infrared microscopic investigation of the distribution of nickel atoms in silicon additionally doped with Holmium.

It was found that during heat treatment in Si <P, Ho> samples, nickel atoms are clearly deposited around the stress fields of the clusters of Holmium atoms. Therefore, the stability of parameters of Si (ρ and τ) doped with Holmium during heat treatment is explained by the active capture of defects and impurity atoms by clusters of Holmium atoms.

The above experimental results show that Holmium atoms in interstitial unstable states in the lattice tend to migrate to a more energetically favorable state, i.e., to a quasi-equilibrium state in the process of low-temperature doping, thus interact and further form clusters. Meanwhile, the crystal eliminates single Holmium atoms, and the system goes into the most energetically favorable state. The formation and interaction of clusters due to Holmium atoms, significantly removes the strain stress in the crystal. The main stimulant is both oxygen atoms and other lattice defects, respectively. Clusters of impurity atoms of Holmium manifest significant guttering effect that in turn significantly reduces the concentration of uncontrolled contaminant crystal impurities and inhibits the formation of thermal

donors.

CONCLUSION

The authors present the phased low-temperature diffusion technology of doping of silicon with Holmium, which ensures formation of clusters of impurity atoms of Holmium uniformly distributed throughout the crystal bulk. The presence of such clusters allows not only controlling the properties of a semiconductor material, but also allows one the use of such materials in the development of novel types of solar cells. The results of a study of the surface of samples after diffusion showed that, no surface erosion or formation of alloys and silicide on the surface are detected while applying low temperature diffusion technology which normally takes place during high-temperature diffusion doping. It has been revealed that during phased low-temperature diffusion process, the temperature and diffusion time affect not only the penetration depth of the impurity, but also the size of the formed clusters.

A comprehensive study of the physical properties of silicon containing ordered clusters of impurity atoms of Holmium can contribute to the discovery of novel physical phenomena that were not found previously in doped semiconductor materials. The study also could help to discover new phenomena in semiconductors with nanostructures. Possibility of controlling the state and distribution of clusters of impurity atoms of Holmium in the silicon crystal lattice allows us to create a new class of semiconductor material with unique functional capabilities, as well as to create a new class of devices for optoelectronics, microelectronics, and solar energy on its basis. An analysis of the studies and the results obtained during experiments to engineer clusters of impurity atoms of Holmium atoms have clearly shown that it is possible to enforce migration of the resulting clusters to the desired place in the material.

It has been established that Si <P, Ho> samples are characterized by enhanced thermal and radiation resistance parameters. The silicon doped with Holmium significantly stabilizes the lifetime of minority charge carriers during additional thermal annealing. The material is also characterized by increased radiation resistance when exposed to γ -irradiation. It could also be concluded that the formation of clusters of impurity atoms of Holmium has a strong gettering effect.

REFERENCES

1. Bagraev N.G., Romanov V.V. Magnetism of AIII BV crystals doped with rare elements. FTP, 2005, T.39, v.10, pp. 1173-1182.
2. Suzdalev I.P. Nanotechnology: physical chemistry of nanoclusters, nanostructures and nanomaterials. M.Kom Book, 2006. 592s
3. Bakhadyrhanov M.K., Sodikov U.X., Melibayev D., Wumaier Tuerdi, Koveshnikov S.V., Khodjanepesov K.A., Jiangxiang Zhan Silicon with Clusters of Impurity Atoms as a Novel Material for Optoelectronics and Photovoltaic Energetics // Journal of Materials Science and Chemical Engineering, 2018, 6, 180-190.
4. Egamberdiev B.E., Iliev Kh.M., Nasriddinov S.S., Toshev A.R., Zoirova M.E. Photoelectric properties of silicon- based solar cells implanted with rare earth elements. // Conference. Russia, Vladivostok, 2006. PP. 204-208.
5. Abdurakhmanov B.A., Egamberdiev B.E., Iliev H.M., Tachilin S.A., Toshev A.R. "The effect of silicon – germanium microheter junctions on the parameters of silicon solar cells" //

THE MULTIDISCIPLINARY JOURNAL OF SCIENCE AND TECHNOLOGY

VOLUME-5, ISSUE-4

Journal of Electronic Materials Processing, Moldova, 2010, No. 5, p. 124-126.

6. Egamberdiev B.E., Iliev H.M., Tachilin S.A., Toshev A.R. "Radiation Stability of Holmium Doped Silicon Solar Cells" // XI International Conference "Solid State Physics" Ust-Kamenogorsk, Kazakhstan, June 9-12, 2010
7. Bahadyrkhanov M.K., Iliev H.M., Khamidov A., Toshev A.R. "The degradation properties of silicon solar cells with rare earth impurities" // Solar technology 2002, No. 3, pp. 19-22.
8. Daliev H.S., Utamuradova Sh.B., Daliev Sh.Kh., Dekhkanov M.Sh., Norkulov Sh.B. About the influence of dysprosium on the processes of radiation defect formation in silicon // Uzbek Journal of Physics. Vol. 20 (No. 2). 2018. pp. 131-133.
9. Ayupov K.S., Bobonov D.T., Zikrillaev N.F., Saparniyazova Z.M., Toshev A. low-temperature diffusion of impurities in silicon // Doklady AN Academy of Sciences of the Republic of Uzbekistan. - Tashkent, 2010. - No. 4.– S. 34- 38.
10. Dipak Malpure Rajaram, Sharada Deore Laxman. "Buccal Mucoadhesive Films: A Review." Systematic Reviews in Pharmacy 8.1 (2017),31-38.
Print. [doi:10.5530/srp.2017.1.7](https://doi.org/10.5530/srp.2017.1.7)