Materials Science in Semiconductor Processing 74 (2018) 165–169

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Boron-doped hydrogenated mixed-phase silicon as thermo-sensing films for infrared detectors

Duy Phong Pham[a], Jinjoo Park[a], Chonghoon Shin[b], Sangho Kim[b], Yonghyun Nam[c], Geunho Kim[c], Minsik Kim[d], Junsin Yi[a,*]

[a] College of Information and Communication Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea
[b] Department of Energy Science, Sungkyunkwan University, Suwon 440-746, Republic of Korea
[c] SIRIUS. Inc, 385, Expo-ro, Yuseong-gu, Daejeon 34051, Republic of Korea
[d] The Department of Electrical Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong – Gu, Daejeon 34141, Republic of Korea

ARTICLE INFO

Keywords:
Micro-bolometers
Infrared detectors
Boron-doped
Hydrogenated silicon films

ABSTRACT

Silicon materials have been widely used as thermo-sensing layers in infrared detectors or uncooled micro-bolometers. Parameters such as a large thermal coefficient of resistance (TCR), low sheet resistance (R_s), and low 1/f noise are important for high performance of these devices. However, there is always a trade-off between these parameters. For example, the crystalline silicon materials typically exhibit low R_s and 1/f noise, and significantly low TCR, while the amorphous silicon materials generally have large TCR, and considerably high R_s and 1/f noise. Consequently, the best trade-off can be achieved by using a mixed-phase structure of silicon materials, i.e. an intermediate form between the crystalline and amorphous structures. Herein we report the important characteristics of hydrogenated mixed-phase silicon films, deposited by the plasma-enhanced chemical vapour deposition process, for infrared detectors. The films in the mixed-phase structure showed high TCR values in the range of 2–3% K^{-1} and moderate sheet resistances in range of 10–40 MΩ sq^{-1}. These results indicate that the mixed-phase silicon films are potential alternatives to conventional boron doped hydrogenated amorphous and microcrystalline silicon films for use as thermo-sensing layers in infrared detectors.

1. Introduction

Uncooled infrared detectors, which are also known as uncooled micro-bolometers, have generated considerable interest in recent years owing to their advantageous attributes such as wide spectral response, low cost, and light weight [1]. They have been used for a wide range of applications such as security survey systems, biomedical thermography, military night vision, and for fire detection [2,3]. These devices operate on the principle that the resistivity of their constituent materials exhibits a large temperature dependence. This means that the electronic properties such as conductivity or resistivity of the device change with rising temperature of the thermo-sensing materials upon infrared (IR) radiation absorption [4]. With regard to their thermo-sensing applications, the essential material characteristics that promote device performance include low electrical noise, large temperature coefficient of resistance (TCR, which estimates the IR sensitivity of the material), and low electrical resistivity (useful for determining compatibility with read-out circuitry) [5,6]. Several materials such as amorphous silicon (a-Si:H), vanadium oxide, and some metals have been suggested for commercial micro-bolometer arrays. Even though these materials have been used as commercial micro-bolometer arrays, they still have many limitations which need to further improve. For example, the metals used for the device can be compatible with standard silicon complementary metal-oxide semiconductor (CMOS) fabrication, but they seem to suffer from substantially low activation energy (E_a) and thus exhibit a significantly low TCR [7]. Although vanadium oxide demonstrates a high TCR (around 2–3% K^{-1}), it is not compatible with CMOS technology and generates a high noise (1/f noise) because of its non-crystalline structure [8]. Finally, despite having considerable advantages such as a high TCR and compatibility with silicon CMOS technology, a-Si:H films exhibit significantly high resistivity, which leads to an incompatibility with the CMOS read-out circuits [9].

In order to achieve a balance between TCR and resistivity, mixed-phase structures of silicon materials have been extensively investigated in recent years [3,6,10,11]. Such a structure can be obtained by modifying the deposition conditions and parameters. It is defined as an intermediate structure between the crystalline phase form and the amorphous phase of silicon materials. The silicon material in such a

* Corresponding author.
E-mail address: yi@yurim.skku.ac.kr (J. Yi).

http://dx.doi.org/10.1016/j.mssp.2017.10.034
Received 19 August 2017; Received in revised form 8 October 2017; Accepted 22 October 2017
1369-8001/

structure contains several nano- or micro-crystalline grains (around 2–5 nm) distributed in the amorphous matrix [12]. Based on the form of these nano-crystalline grains, the densities of the states or defect densities in films can be reduced and the electric properties as well as stability of the films can be improved [13,14]. In these aspects, the mixed-phase structure of silicon films can be considered as a potential material for replacing a-Si:H as a thermo-sensing film in micro-bolometer devices.

Consequently, in this work, we introduced changes in the structure of silicon films from its crystalline form to the amorphous state by varying the boron doping deposition parameter over a large range. During this change, the mixed-phase structure was detected. The changes in the structure of the films was characterized by Raman and Fourier transform infrared (FTIR) spectroscopies. We performed a thorough analysis of the electrical and thermo-sensing characteristics of the films by considering parameters such as dark conductivity (σ_d), TCR, activation energy (E_a), and sheet resistance (R_s), which are the most important parameters for infrared detectors.

2. Experiment

Boron-doped hydrogenated silicon films were deposited using standard radio frequency (RF – 13.56 MHz) plasma-enhanced chemical vapour deposition (PECVD). The films were deposited from a mixture of silane (SiH_4), hydrogen (H_2), and diborane (B_2H_6) gas flow. The ratio of B_2H_6 to SiH_4 gas flows were varied in a large range from 0.002 to 0.012. The deposition parameters including substrate temperature, power, working pressure, and gas flow ratios are summarized in Table 1. The film thickness of samples, inferred from the fitting of spectroscopic ellipsometry (VASE, J. A. Woollam, in range of 240–1700 nm wavelength), was fixed at around 100 nm.

Raman spectroscopy was used to characterize the nanostructure of the films. Raman spectra were examined in the backscattering configuration using Dongwoo Optron-Ramboss 500i Micro Raman system with an Ar^+-ion laser source having the excitation wavelength of 514 nm. Based on the Gaussian curve fitting of the Raman spectra, the crystalline volume fractions (X_c) were defined based on the formula: $X_c = (I_{520} + I_{510}) / (I_{520} + I_{510} + I_{480})$, where I_{520}, I_{510}, and I_{480} are the integrated areas obtained from Gaussian fitting at 520, 510 and 480 cm^{-1}. The FTIR spectral measurements were implemented for samples deposited on silicon wafer substrates. Based on the FTIR spectra, the microstructural characterizations, so called microstructure factors (R), were determined using the formula: $R = I_{2100} / (I_{2100} + I_{2000})$, where I_{2100} and I_{2000} are the integrated areas obtained from Gaussian fittings at 2100 cm^{-1} and 2000 cm^{-1}, respectively. The room temperature dark conductivity (σ_d) of the samples was measured with a couple of evaporated coplanar metal aluminium electrode (250 µm spacing) on the surface using Semiconductor Test and Analyzer (model EL420C) system. The sheet resistance of films was inferred from formula: $R_s = 1/ \sigma_d.t$, where t is the film thickness. Based on measurements of temperature dependence of σ_d in range temperature of 300 – 400 K, the activation energy (E_a) values were determined from the slope of the linear fitting of the $\ln(\sigma_d)$ vs. $1/kT$ curve.

Table 1
Deposition parameters of p-uc-Si:H layers.

Parameters	Values
$[H_2]/[SiH_4]$ flow ratio	160
$[B_2H_6]/[SiH_4]$ flow ratio	0.002–0.012
Power density	208 mW/cm^2
Working pressure	1500 mTorr
Deposition temperature	160 °C
Thickness	100 nm

3. Results and discussion

The mixed-phase silicon material is known to be comprised of a phase mixture between amorphous and crystalline states. It can be envisioned as a superposition of the signals from the crystalline and the amorphous phase, to form a so called transition phase region. Generally, the transition region of the silicon materials implemented by PECVD can be achieved by changing either the hydrogen dilution, which is also known as $[H_2]/[SiH_4]$ flow gas ratio, or varying other conditions such as plasma power, substrate temperature, pressure, excitation frequency, and electrode spacing [15–17]. However, the aim of this study was to obtain mixed-phase silicon films with a high carrier concentration (i.e. high conductivity) in order to significantly reduce the 1/f noise value. The 1/f noise or low frequency noise is an important parameter of uncooled micro-bolometer devices. Conventionally, the 1/f noise value of a material can be expressed by Hooge's experimental formula [18,19]: $S_I = \alpha.I^2/N.f$, where S_I is the power density spectra, I is the bias current, N is the total number of charge carriers, α is the noise or Hooge parameter and f is frequency. This formula indicates that the 1/f noise is inversely proportional to the number of total free carriers and proportional to Hooge parameter (α), which depends on the quality of crystalline and mobility of carriers [20]. This means that a high carrier concentration, as well as high crystalline level of thermo-sensing films, is supposed to low 1/f noise value. Consequently, we examined the effect of varying boron doping ratio, as the $[B_2H_6]/[SiH_4]$ gas ratio, on the conductivity of the films. A wide-ranging variation in doping can result in a considerable change in the lattice structure of silicon materials, from its amorphous to crystalline state, and the transition region can be detected based on this study [21,22]. One of the most convenient and reliable methods to detect this mixed state region of silicon materials is Raman scattering. It is well-known that the amorphous phase of these materials corresponds to the Raman spectrum signal at 480 cm^{-1} and the crystalline phase can be attributed to the signals in the range of 500–520 cm^{-1}. Fig. 1a–c illustrate the Raman spectra of films as a function of the $[B_2H_6]/[SiH_4]$ flow gas ratios. As seen Fig. 1a, with the gas ratios below 0.005, the Raman spectra showed the crystalline phase with strong and sharp transverse optic (TO) peaks centred at 520 cm^{-1}. In contrast, Fig. 1c clearly shows the characteristic wide peaks of the amorphous phase at 480 cm^{-1} when the gas ratio was over 0.008 as a result of the disorder induced changes in the vibration density of the states. This indicated that the film structure was transformed from the highly crystalline phase to amorphous phase with the wide-range gas ratio variations. Particularly, in the range of the gas ratios from 0.006 to 0.007, the Raman spectra clearly showed the mixed-phase region with a downward shift in the intensity of the peak corresponding to the crystalline state at 510 cm^{-1} and a broadening of the peaks located at 500 and 480 cm^{-1} probably caused by the phonon confinement effect [23–26]. The Gaussian curve fitting shown in Fig. 1d clearly illustrates the presence of three peaks, of which the peaks at 500–510 cm^{-1} is attributed to the intermediate phase between the amorphous and microcrystalline states [26,27].

Based on the Raman spectra, the crystalline volume fraction of the films was calculated as shown in Fig. 2a. In addition, the structure fraction, extracted from FTIR spectroscopic data, is presented in Fig. 2b. Fig. 2a shows the gradual decrease in X_c with the increasing gas ratios. This general trend has also been observed by other groups [22,28]. These results indicate that high boron-doping remarkably reduces the crystalline fraction of the films. In order words, a high content of the boron dopant results in a higher density of defects and as a result, the film structure becomes more disordered. The increasing defect density because of doping is also illustrated by the gradual increase in the microstructural parameters (R), as shown in Fig. 2b. It is evident that the variations over an extensive range of boron doping can considerably change the structure of the silicon films from the crystalline to amorphous phase, from which a mixed-phase region can be detected